Study of some marine bivalves as the biomonitor candidates for environmental assessment of the Jiaozhou Bay by NAA and AAS^{*}

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Abstract Some kinds of marine bivalves were selected as the biomonitor candidates to study the possibility of the environmental assessment of the Jiaozhou Bay with biomonitors. The contents of 29 elements in bivalve samples were determined by neutron activation analysis and atomic absorption spectrometry. It is found that clam is a suitable kind of marine bivalves as a biomonitor to evaluate the environmental quality of the Jiaozhou Bay. The environmental status of some sampling sites in this marine area was tentatively assessed by the biomonitors of calm and mussel.

Keywords Biomonitor, Marine bivalves, Environmental assessment, Neutron activation analysis, Atomic absorption spectrometry

1 Introduction

The district of the Jiaozhou Bay in the eastern China is an example of highly anthropogenic resulted complex ecosystem which merges multi-functions of industries, agriculture, commerce, life, transportation, tourism and so on into an integral whole. It is interesting to use biomonitors for environmental assessment of this important marine area. The study of biomonitors is also one of the major goals in our first pilot Chinese Biological Environmental Specimen Bank (CBESB), which has been operating in the Laboratory of Nuclear Analysis Techniques, the Chinese Academy of Sciences. The status of CBESB was described in our previous paper.^[1]

It is well known that collection and analysis of biomonitor samples have many advantages over abiotic samples in environmental studies, including bio-concentration of pollutants, relatively simpler sampling techniques, more relevant to the biological significance, and getting the information of integrated exposure over a time period. Now more and more scientists use biomonitors to assess the status of various ecosystems. For example, lichen and moss are quite suitable as biomonitors to evaluate air pollution^[2,3] and mussel is often used as a biomonitor to asses limnetic and marine ecosystems.^[4,5] Markert *et al.* reviewed some general aspects of heavy metal monitoring by plants and animals.

Some sorts of marine bivalves were collected at three sites of the Jiaozhou Bay. The contents of multi-elements, including biologically essential and toxic ones, have been determined by instrumental neutron activation analysis (INAA) and atomic absorption spectrometry (AAS). The ultimate purpose of our work is to identify what kind of marine organism is the optimal biomonitor and which elements can be served as the target components to evaluate the environmental status of this special marine system. The preliminary results and the resulting perception are introduced in the present paper.

2 Materials and methods

About 1 kg of each kind of marine bivalves, clam (Ruditapes philippinarum), mussel (Mytilus galloprovincialis) and oyster (Ostrea denselamellosa), were collected at the different intertidal zones of the three sites, which were Shuang-Pu (SP), Tuan-Dao (TD) and Huiquan-

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Jiao (HJ), in the Jiaozhou Bay during November of 1996. Fig.1 shows their sampling locations. All the collected marine organisms were rinsed thoroughly with sea water in situ, and afterwards three times rinsed with deionized water. The rinsed samples were packed into clean polycthylene bags, and then stored temporarily in a refrigerator at -20° C. All the sample containers and package materials were acidsoaked, tap water and deionized water rinsed in advance. The samples were transported to CBESB Laboratory in Beijing with a portable ice box, and then stored at -70° C until the preparation for analysis.



Fig.1 Sampling sites (0) in the Jiaozhou Bay

When a batch of stored bivalve samples was taken out for analysis, the contents of soft tissues were scooped out with titanium implements in a class 100 clean room, then temporarily stored in a freezer and ready for freezedrying. The freeze-dried materials were ground and homogenized with a micro-dismembrator. The shaking flask is made of high purity teflon and the grinding balls are teflon-coated steel ones. For getting large enough amount of powder samples an agate pestle and mortar was also used for homogenization. About 50 mg and 150 mg of the powder samples were weighted as subsamples used for short-time and long-time irradiation, respectively.

The contents of elements Al, Au, Ba, Br, Ca, Ce, Cl, Co, Cr, Cs, Eu, Fe, I, K, Mg, Mn, Na, Rb, Sc, Se, Sm, Sr, Th, V and Zn in marine bivalve samples were determined by INAA, and the contents of elements As, Cd and Pb were determined by AAS. Some certified reference materials (CRMs), Mussel (GBW08571) and poplar leaves (GBW07604) were used for analytical quality control.

The samples, CRMs and comparator standards were sealed in polyethylene capsules for irradiation. The short-time and long-time irradiation were carried out in a pneumatic transfer system in the miniature neutron source reactor (MNSR) at China Institute of Atomic Energy. The basic conditions for INAA are listed in Table 1. A heated graphite-furnace atomizer coupled to an atomic absorption spectrophotometer was used for atomic absorption measurement.

Thermal neutron flux $/n \cdot cm^{-2} \cdot s^{-1}$	Irradiation time	Decay time	Counting time	Measured nuclides
2×10 ¹¹	1~5 min	1~5 min	3 00 s	²⁸ Al, ⁸⁰ Br, ⁴⁹ Ca, ³⁸ Cl, ¹²⁸ I, ⁴² K, ²⁷ Mg, ⁵⁶ Mn, ²⁴ Na, ⁵² V
6×10 ¹¹	26 h	10~ 16 d	6000∼40000 s	

Table 1 Basic conditions for neutron activation analysis

3 Results and discussion

Clam, mussel and oyster are three major kinds of marine bivalves in the Jiaozhou Bay. Among the 29 elements we analyzed, the elements of Eu, I, K and V in bivalve samples were not discussed in the following because of their contents closer or lower than detection limit. Major elements Na and Cl were also not discussed. Fig.2 shows the comparison of elemental contents in clam and oyster collected at the low intertidal zone of SP (L-SP). It is found that the contents for most of elements, especially for Al, Ba, Ca, Ce, Co, Fe, Sm, Th, etc., in clam are higher than those in oyster though both collected from the same site. Fig.3 shows the comparison of mussel and oyster, both collected at the middle intertidal zone of TD(M-TD). It is found that the contents for most elements we

analyzed do not show any significant difference. The only exception is that oyster contains much more Zn and mussel contains more Br, Mg and Sr. It is noticed that oyster is particularly rich in zinc, over ten times higher than that in clam and mussel. Because of the difficulty to find all these three kinds of bivalves in one site it is impossible to make the comparison of elemental contents among clam, mussel and oyster. From the results shown in Figs.2 and 3, we suggest that clam is a suitable kind of marine organism as a biomonitor in the Jiaozhou Bay, besides its higher bio-concentration ability for many elements it is also a major marine product in this marine area and easy for sampling. For worldwide marine environmental assessment, mussel may be more suitable as a biomonitor because its habitats are more widespread.



Fig.2 Elemental contents of clam and oyster in L-SP



Fig.3 Elemental contents of mussel and oyster in M-TD

While using clam as biomonitor to observe the difference of environmental status between the middle intertidal zone of SP (M-SP) and low intertidal zone of SP (L-SP), there is no significant difference for the contents of most analyzed elements except Al, As, Br, Ca and Th (Fig.4). The contents of elements Al, Ca and Th in L-SP are higher than those in M-SP, but As and Br are in contrary. It is reasonable that the two different intertidal zones in SP are in a similar level of environmental status.

While using mussel as a biomonitor, it can be seen from Fig.5 that there are quite a few elements, such as Al, Br, Ca, Ce, Mg Mn and Sr, their contents in M-HJ are higher than those in M-TD. It may result from the fact that HJ is a tourism spot in the Jiaozhou Bay and result in a little more contaminated than TD.



Fig.4 Elemental contents of clam in M-SP and L-SP



Fig.5 Elemental contents of mussel in M-TD and M-HJ

As searching for the suitable elements served as target components to assess the environment quality it is necessary to accumulate more knowledge on the effect of environment on the characteristics of the selected organisms. For our preliminary results, it seems that elements As, Br in clam and Br, Mn, Sr in mussel, etc., probably are the characteristic elements for the assessment of environmental pollution in the Jiaozhou Bay.

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