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EVALUATION OF ACID VOLATILE SULFIDE (AVS) DISTRIBUTION IN TIDAL MUD OF THE ARIAKE SEA, JAPAN

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ABSTRACT: *A remarkable decrease of catch of shells was observed during the last three decades in the Ariake Sea. The higher content of acid volatile sulphide (AVS) is responsible for the unfavourable geoenvironmental condition. In this study, the relationship between the thermal properties of the tidal mud and the AVS is evaluated. The tidal mud was collected from Iida and Higashiyoka tidal flat in the Ariake Sea by using a 90 cm length and 7 cm diameter steel tube sampler. Thermal properties were measured by using the digital thermal properties analyser and the AVS was measured by using the GASTEC 201 H/L method at pre-determined depths in the laboratory. It is found that the AVS value shows peak at the same depth where the volumetric heat capacity value shows the peak. A modification is proposed in the classic depth distribution of AVS in the marine sediments by including the thermal properties of the tidal mud.*

KEYWORDS: Ariake Sea, Avs, Sulphate Reducing Bacteria, Tidal Flat, Thermal Properties, Volumetric Heat Capacity

INTRODUCTION

The Ariake Sea, which is located in the south-western part of Kyushu Island, is one of the best-known semi-closed shallow seas in Japan. Many rivers flow into the eastern coast area of the Ariake Sea and carry 4.4 x 10^8 kg of sediments per year (Azad et al. 2005). Coarse sediments accumulate in the eastern coast, and fine grains brought by the residual current accumulate in the bay head to form vast tidal flats with fine sediments (Kato and Seguchi 2001). The vast tidal flat mud of the Ariake Sea, which is almost 40% of the total tidal flat area of Japan, is famous for its rich fishery products and *Porphyra* sp. (sea weed) cultivation. Different types of shells like *Sinonovacula constricta*, *Atrina pectinata* and *Crassostrea gigas* are important creatures in the Ariake tidal mud. However, a dramatic decrease of these shells is observed in the tidal flat area. For example, the catch of *Crassostrea gigas* usually living in the near surface mud, dropped from 7.99 x 10^5 kg in 1976 to only 1.26 x 10^5 kg in 1999; that of *Atrina pectinata,* living in the upper 0.10-0.15 m of the mud, declined from 1.3395 x 10^7 kg in 1976 to 7.9 x 10^4 kg in 1999, and the situation in the case of *Sinonovacula constricta*, living in the depth of 0-0.7 m of the mud, was even worse: 1.7 x 10^5 kg catch in 1976 dropped to practically nil by 1992. The acid treatment practice for *Porphyra* sp. cultivation is one of the major causes for this declination of the shells as this practice has made the geo-environmental condition of the Ariake tidal mud unfavourable for the living creatures of the tidal mud (Moqsud et al. 2007). The high value of AVS is the main responsible thing to make the geoenvironmental condition unfavourable. The sulphate reducing bacteria is an important stuff to reduce the sulphate compounds to sulphide compounds. Again, the activities of the sulphate reducing bacteria largely depend on the thermal environment of the tidal mud. The sequestration of sulphur within sedimentary pyrite is a major sink in the global biogeochemical sulphur cycle. In many

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sedimentary environments, a zone exits which releases hydrogen sulphide if treated with acid. The materials that produce this sulphide described as acid volatile sulphide (AVS) (Rickard and Morse 2005).

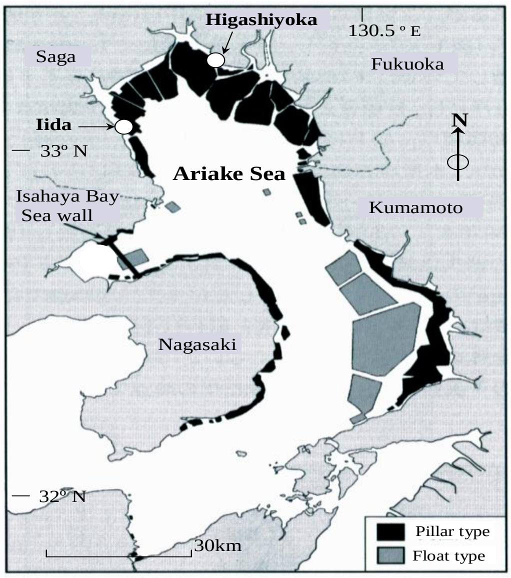

Figure.1 Map of the Ariake Sea indicating the study areas and different types of *Porphyra* sp. cultivation areas

Thermal properties refer to the properties of a material which is related to temperature and the volumetric heat capacity is the properties of a matter which implies the amount of energy required to increase or decrease one degree Celsius temperature. In this paper, an innovative relationship between the AVS distribution and the volumetric heat capacity of the tidal mud is discussed and consequently proposed a new AVS-depth distribution method and a sulfur cycle in the Ariake Sea by incorporating the thermal properties.

Sampling Sites

Two tidal flat areas in the Ariake Sea, Iida and Higashiyoka were selected for sampling the mud. Figure 1 shows the map of the Ariake Sea indicating two sampling areas. The tidal currents sweep into the sea and move northwards along the eastern shoreline and create a counterclockwise water movement. Before selecting the study areas, field investigations were undertaken. Higashiyoka, located in the bay head was chosen as a study area, which is near to Chikugo river (the biggest river in Kyushu Island), Okinahata river as well as other rivers. Another study area was Iida, which seems to be more affected by the acid treatment practice. The mud samples at the Iida site gave out a strong unpleasant odor due to the gas-phased hydrogen-sulfide (H_2S), whereas the mud samples of the Higashiyoka site did not have such odor. The typical values of the basic physicochemical properties of the Iida and Higashiyoka tidal mud are tabulated in the Table 1.

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MATERIALS AND METHODS

Laboratory tests were conducted to evaluate the thermal properties at the controlled room temperature at 20 ^{0} C. In-situ samples were collected by inserting vertically a thin wall steel tube sampler with a diameter of 0.07 m and a length of 0.90 m at Iida and Higashiyoka sites during May 2006. For sample collection from tidal flat region an amphibious ship was used. The mud samples from tidal flat were collected during the ebb tide and about 40 m distance from the shore line. The sample was then sliced into 0.05 m layers in the laboratory to measure the thermal properties in each layer. The thermal properties analyser KD2 Decagon Devices, Inc. was used to measure the thermal properties. Briefly, the measurement was done by inserting the needle completely into the samples. The KD2 sensor needle contains both a heating element and a thermistor. The controller module contains a battery, a 16-bit microcontroller /AD converter, and power control circuitry. When the measurement begins, the microcontroller waits for 90 seconds for temperature stability, and then applies a known amount of current for 30 seconds to a heater in the amount of power supplied to the heater. The probe's thermistor measure the changing temperature for 30 seconds while the microprocessor stores the data. At the end of the reading, the controller computes the thermal conductivity and diffusivity using the change in temperature and time data. The data of thermal conductivity and thermal diffusivity are shown directly in the digital display of the thermal properties analyser. The volumetric heat capacity was calculated by dividing thermal conductivity by thermal diffusivity. The sulphide content was measured following the standard method prescribed by the Japan fisheries resource conservation association. The instrument which is used to measure the sulphide content is the GASTEC 201L/H which was also used by Wu et al. (2003) to determine the sulphide content of the marine sediments. Briefly; measuring sulphide content consists of placing 0. 1 g of mud at field moisture content on a fine porous disk placed in a 1x10^{-5} m^3 glass tube. Then 2 x 10^{-6} m^3 of diluted sulphuric acid (H_2SO_4) (1x 10^{-6} m^{3}of distilled water mixed with 1x 10^{-6} m^3 of 18 N H_2SO_4) was mixed on the mud sample, and the generated H_2S gas was collected. The weight of H_2S was measured and expressed as mass of gas per unit mass of the mud.

Table 1: Basic physicochemical properties of Iida and Higashiyoka tidal mud in the Ariake sea

Physico-chemical parameters	Iida tidal mud	Higashiyoka tidal mud
Density (x 10^{-3} kg/m^3)	2.69	2.71
Water content (%)	235	168
Liquid limit w_L	150	130
Plasticity Index Ip	87	73
Ignition Loss (%)	13.3	11.9
pH	7.92	8.03
ORP (mV)	-121.4	98
AVS (x 10^{-3} kg/kg dry-mud)	0.42	0.16
Salinity (x 10^{-3} kg /m^3)	16	17
Grain size analysis (%)		
Sand	10	10
Silt	30	45
Clay	60	45

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RESULTS AND DISCUSSION

Relation between Volumetric Heat Capacity and AVS Maximum Depth

From Fig. 2 it is seen that the volumetric heat capacity shows a higher value in the depth of 5 to 25 cm at the same time the AVS values are also showed higher value in those zone. The AVS is produced by the activities of the sulphate reducing bacteria. This special zone of higher AVS production is also the same zone of higher volumetric heat capacity. This type of trend is probably due to the higher concentration of SRB in that zone. As the higher volumetric heat capacity zone is more stable condition in terms of thermal environment and the living organism of SRB like this zone very much for their comfortable living. From an unpublished data of SRB concentration in different layers in the Ariake Sea tidal flat, it is also seen that the higher concentration of SRB and the higher AVS zone are in the almost same depth. If the same condition is maintained in the different layers, the sulphate reducing bacteria will be more in that layer where it is more stable in terms of temperature change or more specifically the higher volumetric heat capacity region.

Proposed Modification of AVS-Depth Distribution

Figure 3 shows that the modified AVS–depth distribution profile in the marine sediments. The previous AVS- depth distribution was developed by Sorensen and Jorgensen (1987) in terms of chemical condition. Now the AVS-depth distribution is proposed in terms of thermal properties. In the classical depth distribution of AVS, it is seen that there is a zone (zone 2) where the rapid generation of AVS is observed. This zone that produces the AVS is generally the black material, classically situated just below the sediment-water interface. This zone 2 in the classical AVS depth distribution is projected to be modified in this study in terms of thermal properties i.e. the zone 2 is also proposed as the higher volumetric heat capacity zone.

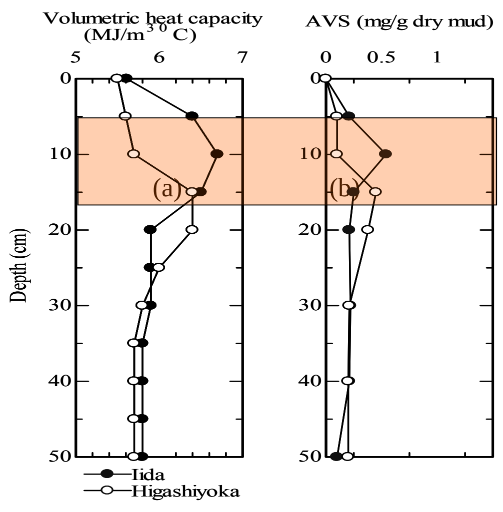

Figure. 2 Variation of a) volumetric heat capacity and b) AVS with depth in the Ariake sea tidal flat

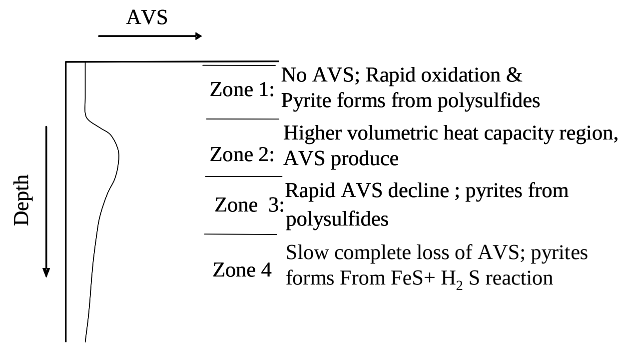

Fig. 3 Proposed modification of AVS depth distribution by incorporating thermal properties in the muddy tidal flat

Conceptual Image of Sulphur Cycle in the Ariake Sea

Figure 4 illustrates the conceptual image of the sulphur cycle in the study area. Generally, the sequestration of sulphur within sedimentary pyrite is a major sink in the global biogeochemical sulphur cycle and has consequent impacts on the related cycles of carbon and oxygen. One of the controlling aspects of the interrelated global biogeochemical cycles of carbon, oxygen and sulphur is the removal of sulphur from the ocean-atmosphere system and its burial in sediments. In this conceptual image of sulphur cycle of the Ariake sea, it is seen that the sulphur cycle of the Ariake sea is disturbed by some additional chemical materials of sea laver treatment chemical and the compounds contain in it. Every year almost 3000 ton of sea laver treatment chemicals are dumped into the Ariake Sea by the sea laver cultivators to treat the sea laver. This huge quantity of acid which contains ammonium sulphate $(NH_4)_2SO_4$) and some phosphorus compounds supply ample quantity of foods to the sulphate reducing bacteria. The SRB increase their activities with the favourable living condition of higher volumetric heat capacity zone with the help of ample food supplied. The activity of the sulphate reducing bacteria increases in the increased temperature of (18-37 ^{0} C) during spring and summer. The consequence of the sulphate reducing bacteria's activities is the AVS production and increased concentrations. The sulphate reducing bacteria are the major activist for the sulphide content in the marine sediment. Where the concentration of the sulphate reducing bacteria is high their activity will also high at that region and, consequently, the sulphide content is also high at that area. This causes the unbalance in the sulphur cycle in the Ariake Sea and the AVS values are well above the safe limit for the living creatures in the Ariake sea tidal mud (Moqsud et al. 2007).

CONCLUSIONS

The AVS represents a complex and dynamic biogeochemical system which is not defined simply by analysis of acid volatile sulfide materials. Actually there are many factors which are liable to produce AVS in some specific regions. However, in this study an innovative idea has been adopted to the classical depth distribution of AVS in the tidal flat area on the basis of the continuous sampling from the Ariake sea tidal flat areas and performing test of thermal properties as well as AVS measurement in different depths. The AVS value shows the peak at the depth where the volumetric heat capacity value shows also the peak both at Iida and the Higashiyoka tidal flat mud samples in the Ariake Sea.

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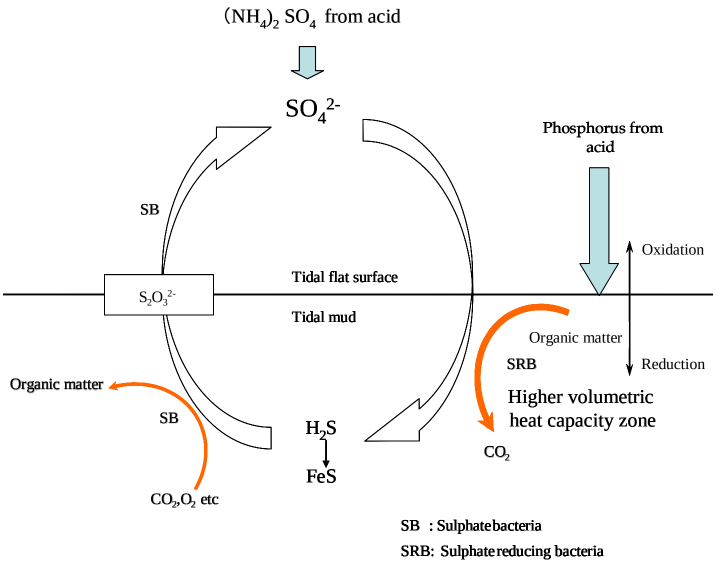

Figure. 4 Conceptual image of sulphur cycle in the Ariake Sea affected by acid treatment practice

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