Annual and Seasonal Trends of Sulphide Content of Tidal Flat Mud in the Ariake Sea, Japan

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Abstract: The high Sulphide Content (SC) of mud is found to be one of the most important causes for unfavorable geo-environmental condition for the benthos in the acid contaminated Ariake Sea, Japan. In order to identify the temporal variation of the sulphide content of the mud, field tests were conducted in the Isida and Hagashiyoka tidal flat mud area of the Ariake Sea during the period 2002-2005. The collected column of mud was cut into a number of specific layers the thickness of which increased with increasing depth. The sulphide content of the mud in each layer was measured along with other physico-chemical properties. The sulphide content of the mud varies from 0.5 to $2.0 \times 10^{-3}$ kg kg$^{-1}$ dry-mud, which is above the allowable limit ($0.2 \times 10^{-3}$ kg kg$^{-1}$ dry-mud) for the favorable condition of the benthos’ life. In summer, the peak value of the sulphide content varies from 1.5 to $2.0 \times 10^{-3}$ kg kg$^{-1}$ dry-mud since the bacterial activities increase with the elevated seasonal temperature. The peak value of the sulphide content, on the other hand, is relatively low ($0.5$-$1.0 \times 10^{-3}$ kg kg$^{-1}$ dry-mud) during the winter as the activities of bacteria as well as bioturbation decrease in the cold temperature. The maximum sulphide content depth was also influenced by the seasonal temperature. The highest sulphide content in the mud that decreases gradually from $2.0 \times 10^{-3}$ kg kg$^{-1}$ dry-mud at 2002 to $1.3 \times 10^{-3}$ kg kg$^{-1}$ dry-mud at 2005 indicates growing favorable conditions for the growth of benthos.

Key words: Benthos, geo-environment, sulphide content, seasonal, tidal mud

INTRODUCTION

The Ariake Sea having a unique feature is one of the best-known semi-closed shallow seas in Japan. The total area of this sea is 1700 km$^2$ with an extended 96 km of the bay axis and an average width of 18 km. 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. (seaweed) cultivation. The tidal height at the flood tide is about 3 m in the bay mouth area and it becomes bigger in the bay head area with the tidal height of 4.5-5.0 m. Many rivers flow into the eastern coast area of the Ariake Sea and carry $4.4 \times 10^9$ 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). Environmental issues related to the Ariake Sea have been a topic of increasing interest recently and analysis of characteristics of tidal flats is of great interest to the regional population (Cyranski, 2001; Zhang et al., 2004). Moreover, a dramatic decrease in the catch of the shells, such as Sinonovacula constricta, Atrina pectinata and Crassostrea gigas is observed in the tidal flat mud area. Figure 1 shows that the catch of Crassostrea gigas, usually living near the surface of mud, dropped from 7.99 $\times 10^7$ kg in 1976 to only 1.26 $\times 10^7$ kg in 1999; that of

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Fig. 1: Variation of catch of shells in the Ariake Sea during last three decades. (Source: Saga Agricultural and Forestry Statistical Society, Japan, 2006)
Atrina pectinata, living in the upper 0.10-0.15 m of the mud, declined from 1.3\times10^7 kg in 1976 to 7.9\times10^6 kg in 1999 and the situation in the case of Sinonovacula constricta, living in the depth of 0.70 m of the mud, was even worse: 1.7\times10^7 kg catch in 1976 dropped to practically nil by 1992. The exact causes for the decline of the fisheries products are still unknown. The probable causes, which are argued for this declaration of the fishery catch include: (1) the water quality in the Ariake Sea is deteriorated due to the exchange of water with the rivers causing eutrophication and consequently resulting an enormous evolution of red tide and plankton, (2) man-made changes, such as the Ishahaya bay sea wall construction, started in 1998 caused smaller tide ranges, which resulted in a decrease of mixing efficiency and oxygen depletion of the sea water (Araki et al., 2002; Yamanishi et al., 2002; Koga et al., 2003) and (3) the deteriorated environment in the mud of the Ariake Sea contributed to the decline (Hayashi and Du, 2005). The third aspect is from the questionnaires of the Kyushu local fishermen. The questionnaires reveal that most fishermen thought that the mud in the tidal flat areas of the Ariake Sea has been deteriorated, accompanying the observation that unpleasant odor from the mud was found in the Ariake sea tidal flats. It is thought by the local fishermen that the observed unpleasant odor was toxic and harmful to the Sinonovacula constricta and Atrina pectinata shells. Acid treatment practice for Porphyra sp. cultivation is one of the most probable causes for the mud deterioration (Moqoud et al., 2006). The acid treatment practice increases the sulphide content in the mud which is very much harmful for the benthos living in the tidal mud (Hayashi and Du, 2005). According to Japan fisheries resource association (2002), the safe value of sulphide content for the benthos in the mud is 0.2\times10^{-3} kg kg^{-1} dry-mud. If the sulphide content becomes higher than that of the safe value, various inhabitants of the mud will be in danger. In this study, the results of the variation or trends of the sulphide content in the Ariake tidal muds are presented showing the annual and seasonal variation of the sulphide content in different depths. There are four seasons in Japan. The average monthly temperature in winter ranges from about 7°C (45°F) on the Pacific Coast of Southwest Japan to below-10°C (14°F) in central Hokkaido, while summer monthly average temperatures range from 28°C (82°F) in the southwest to 16°C (61°F) in the north. So, it is seen that the average value of summer and the winter temperature has a great variation in the southern part of Japan where the Ariake Sea is located. The study of geo-environmental condition of the acid contaminated Ariake tidal mud did not get much attention before. But it is very much important to monitor it regularly to restore the damaged marine ecology in the Ariake Sea. This study was carried out from May 2002 to December 2005 to evaluate the annual and seasonal trends of one of the most important parameter for the inhabitants in the tidal mud i.e sulphide content in the Ariake sea tidal mud.

**SIGNIFICANCE OF ACID TREATMENT PRACTICE IN THE ARIAKE SEA**

The acid treatment practice for the Porphyra sp. cultivation is one of the major reasons for the higher sulphide content and consequently bad geo-environmental condition (Hayashi and Du, 2005; Moqoud et al., 2006). The Porphyra sp. belongs to the division Rhodophyta and the product is a favorite food in Japan and Korea. Together with its characteristic flavor, it is rich in nutrients, such as proteins, vitamins, minerals and tasty constituents. More than ten billion sheets of dried Porphyra sp. have been produced in Japan of which Ariake sea accounts for approximately 40% of the total domestic production of this Porphyra sp. (Zhang et al., 2004) that is well known for its high quality. Porphyra sp. is the most important commercial product of the Ariake Sea and it is the main earning source to the huge number of the people in these areas. At present, the Porphyra sp. cultivation area has reached 12-15% of the total area of the Ariake Sea. The total production of Porphyra sp. is about 85 million USD, which is the greatest earning source in the Ariake coast area. Every year the local sea weed farmers start the Porphyra sp. cultivation both pillar type and float type in the Ariake Sea from December. To enable Porphyra sp. cultivation and production, the acid treatment practice has been quickly developed. During the period of the cultivation (December-March), the acid is used as the disinfectant acid to treat the Porphyra sp. cultivated in the sea and also to provide some nutrient phosphorus to it. This acid treatment practice has been widely undertaken all over Japan from 1977 until the present time. In the Kyushu region, the residual acid was directly dumped into the Ariake Sea without any pre-treatment before 2002. According to unpublished data from the Ministry of Agriculture, Forest and Fisheries of Japan, during the period of 1977-2001, annually about 2.9\times10^6 kg of acid was dumped into the Ariake sea water within the Porphyra sp. farming areas. In some regions of Kyushu, such as Saga Prefecture, the direct dumping of acid into the Ariake Sea is being strictly controlled since 2002. The residues of the applied acid are required to be treated to lower its acidity and sufficiently dilute its concentrations before finally being dumped into the.
Ariake Sea and another countermeasure has been taken to reduce the concentration of NaH₂PO₄ from 14 to 4% from 2002. The acid used in the Saga prefecture has the main chemical compositions of 18% of DL-Malic acid (HOOCCHOHCH₂COOH), 15% of ammonium sulphate ((NH₄)₂SO₄), 14% of sodium di-hydrogen-phosphate (NaH₂PO₄), 1% of amino acid and 0.6% of coloring matter. The pH of the acid used in the Saga prefecture is about 2.0.

**EFFECTS OF ACID TREATMENT PRACTICE ON SULPHUR CYCLE IN THE ARIAKE SEA**

Sulphur cycle in aquatic sediments involves both reductive and oxidative process (Jorgensen, 1977, 1990). One important factor controlling the rate of sulphate reduction in sea is the concentration of sulphate (Capone and Kiene, 1988, Sinke et al., 1992) and an enhanced input may stimulate reduction, substantially altering the cycling of elements such as carbon, nitrogen, phosphorus and iron in sediments (Cook and Kelly, 1992). Information on the impact of enhanced sulphate concentration is, however, sparse and the modern phenomenon of a raised atmospheric concentration in acid rain and the discharge of waste water with a high concentration underline the importance of understanding sulphur cycling in sediments (Herlihy et al., 1988; Rudd et al., 1990; Cook and Kelly, 1992; Peiffer, 1998). The potential sources for sulphide content in the marine sediment are mainly the dissolved S(II) species (H₂S, HS⁻, FeHS⁻) which are filter passing and some solid phase of iron sulphide like mackinawite (Fe₆S₈), gogite (Fe₆S₈) and pyrite (Fe₉S₈) (Rickard and Morse, 2005). Figure 2 shows the schematic presentation of sulphur cycle in the Ariake Sea sediment. The oxidation of sulphide, generated by bacterial sulphate reduction, is a key process in the biogeochemical of marine sediments (Jorgensen, 1990). A large amount of organic matter that is deposited on the sea floor along continental margins is oxidized through the bacterial reduction of SO₄²⁻ to HS⁻ (Jorgensen, 1990). Recent radiotracer studies of sulphate reduction combined with mass balance calculations have shown that most (up to 95%) of this HS⁻ is reoxidized to SO₄²⁻ (Jorgensen, 1990). Thiosulphate is an important product of HS⁻ or pyrite oxidation with O₂. The sulphate reduction reaction is as following:

\[
S_2O_3^{2-} + CH₂COOH⁻ + H⁺ \rightarrow 2HS⁻ + 2CO₂ + H₂O
\]  
(1)

and the oxidation of S₂O₃²⁻ correspondingly involves

\[
S₂O₃^{2-} + 8FeOOCOH⁻ + 14H⁺ \rightarrow 2SO₄^{2-} + 8Fe²⁺ + 11H₂O
\]  
(2)

and during S₂O₃²⁻ disproportion, the reaction involves

\[
S₂O₃^{2-} \rightarrow H₂S (Sulphate reducing bacteria)
\]  
(4)

\[
H₂S \rightarrow SO₄^{2-} (Sulphate bacteria)
\]  
(5)

In the Ariake Sea, every year the *Porphyra* sp. cultivators use a huge amount of acid as a disinfectant agent for the sea weed cultivation, which is mainly organic and contains much chemical compounds of SO₄ and phosphorus. The sulphate reducing bacteria use phosphorus as a feed and with a suitable temperature and environment increase their biochemical activities. The enhanced activities of the sulphate reducing bacteria increase the sulphide content in the Ariake tidal mud. Figure 2 shows the schematic diagram of the sulphur cycle in the acid contaminated Ariake Sea. In the presence of sulphate reducing bacteria sulphate is broken down to hydrogen sulphide and on the other hand the sulphate bacteria oxidized H₂S and produce sulphate.

**SAMPLING SITES**

Two tidal flat areas in the Ariake Sea, Iida and Higashiyokka were selected as the study areas. Figure 3 shows the locations of the two sites along with the different types of *Porphyra* sp. cultivation areas. The tidal currents sweep into the sea and move northwards along the eastern shoreline and create a counterclockwise water movement. This would sweep the finer suspended particles delivered by rivers on the east side towards the
was chosen as a study area which is near to Chikugo river (the biggest river in Kyushu island). Okinohata river as well as other rivers and thought to be affected by the river waters. Another study area was Iida (33.57°N, 130.40°E), which seems to be the most 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-sulphide (H₂S), whereas the mud samples of Higashiyoka site did not have such odor. The typical values of basic physicochemical properties of the Iida and Higashiyoka tidal mud are tabulated in the Table 1. The mud samples were collected from the 0-0.2 m in the Ariake tidal mud.

MATERIALS AND METHODS

Test methods: In situ samples were collected by inserting the 0.2 m diameter PVC pipe down in the mud at a depth of 0.2 m and a thin wall tube sampler with a diameter of 0.07 m and a length of 0.90 m at both Iida and Higashiyoka sites in the Ariake Sea, Japan one time in every month during 2002 to 2005. The sample was then sliced into several specify layers in the laboratory (Fig. 4) to measure the sulphide content. Sulphide content is very important geochemical indices to identify the favorable inhabiting conditions of the benthos. The sulphide content was measured following the standard method prescribed by the Japanese Fisheries Resource Conservation Association (JFRCJ) 2000. The instrument which was used to measure the sulphide content was the GASTEC 2011/H (Wu et al., 2003). Briefly; measuring sulphide content consists of placing 0.0001 kg of mud at field moisture content on a fine porous disk placed in a 10×10×10 mm³ glass tube. Then 2×10⁻⁶ m² of diluted sulfuric acid (H₂SO₄) (10⁻⁴ m²) of distilled water mixed with 1×10⁻⁶ m² of 18 N H₂SO₄ was mixed on the mud sample.

Table 1: Basic Physico-chemical properties of Iida and Higashiyoka tidal mud

<table>
<thead>
<tr>
<th>Physico-chemical parameters</th>
<th>Iida tidal mud</th>
<th>Higashiyoka tidal mud</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (x10⁻⁵ kg m⁻³)</td>
<td>2.69</td>
<td>2.71</td>
</tr>
<tr>
<td>Water content (%)</td>
<td>235.00</td>
<td>198.00</td>
</tr>
<tr>
<td>Liquid limit (W%)</td>
<td>150.00</td>
<td>130.00</td>
</tr>
<tr>
<td>Plasticity Index (%)</td>
<td>87.00</td>
<td>75.00</td>
</tr>
<tr>
<td>ignition Loss (%)</td>
<td>15.30</td>
<td>11.90</td>
</tr>
<tr>
<td>pH</td>
<td>7.92</td>
<td>8.03</td>
</tr>
<tr>
<td>ORP (mV)</td>
<td>-121.40</td>
<td>98.00</td>
</tr>
<tr>
<td>Sulphide content (x10⁻³ kg kg⁻¹ dry-mud)</td>
<td>0.42</td>
<td>0.16</td>
</tr>
<tr>
<td>Salinity (g m⁻³)</td>
<td>16.00</td>
<td>17.00</td>
</tr>
<tr>
<td>Grain size analysis (%)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sand</td>
<td>10.00</td>
<td>10.00</td>
</tr>
<tr>
<td>Silt</td>
<td>30.00</td>
<td>45.00</td>
</tr>
<tr>
<td>Clay</td>
<td>60.00</td>
<td>45.00</td>
</tr>
</tbody>
</table>

Fig. 3: Map of the Ariake Sea indicating the study areas and the different types of Porphyra sp. cultivation area

Fig. 4: Sketch of the sampling tube
and the generated H₂S gas was collected. The weight of H₂S was measured and expressed as mass of gas per unit mass of the mud. The sulphide content was calculated using the following equation:

\[
S (\text{mg g}^{-1} \text{ dry-mud}) = \frac{\text{Gastee detection pipe reading} \times 100}{S_1 / S_2}
\]

Where

- \( S_1 \) = Weight of wet sample (g)
- \( S_2 \) = Percentage of dry mud (%)

The data which is not shown in the graph in different months was not measured.

**RESULTS AND DISCUSSION**

Figure 5 shows that the variation of sulphide content with depth during 2002. It is seen that in the sub-surface region (0-0.04 m) the sulphide content is lower than that in the deeper region. As the sulphate reducing bacteria are anaerobic, they do not like the area where oxygen supply is more (Holmer and Stockholms, 2001). In the tidal area when the tide comes it turbulates the sub-surface region and provides plenty of oxygen to the mud, the bacterial activities become slower and consequently produce small quantity of sulphide in the mud. Moreover, the supplied oxygen makes the sulphate from the sulphide in the mud in that region (0-0.04 m) (Jørgensen, 1990). In May, June, July, August, September and October show that the sulphide content was gradually increased up to 0.1 m depth; the sulphide content was gradually decreased with increasing depth. In November and in December, it shows the same trend with a little dissimilarity. Figure 6 shows that the variation of sulphide content with depth in 2003 both at Iida and Higashiyoka site. It is seen that the sulphide content is gradually increased with the increasing depth up to 0.1 m and after that it becomes start to reduce gradually with

![Fig. 5: Variation of sulphide content with depth at Iida and Higashiyoka site in 2002](image)

![Fig. 6: Variation of sulphide content with depth at Iida and Higashiyoka site in 2003](image)
Fig. 7: Variation of sulphide content with depth at Iida and Higashiyoka site in 2004

Fig. 8: Variation of sulphide content with depth at Iida and Higashiyoka site in 2005

respect to depth. But the variation of sulphide content is different during the December. In December, the sulphide content values show a different trend. It was almost nil up to 0.08 m; this is probably due to the water temperature effect of the winter. In the colder temperature (less than 18°C) range, the bacterial activities become slower and the bioturbation is also reduced due to the colder water temperature (Holmar and Storkholm, 2001) and consequently produce small quantity of sulphide in the mud. Figure 7 shows that the variation of sulphide content with depth in 2004 both in Iida and Higashiyoka site. It is seen that during April and May, the sulphide content did not vary up to 0.20 m. But from July, it showed the same trend as 2002 and 2003 variation. In September, October and November it is seen that the sulphide content under the 0.2m depth did not vary much and the values were always under the 0.2×10⁻³ kg kg⁻¹ dry-mud. In 2004, from June to September there were 3 big typhoons in the Ariake Sea. This typhoon created much turbulence in the surface and sub-surface regions of the tidal mud which affect the sulphide content variation trend with respect to depth from the previous months. Figure 8 shows that the variation of sulphide content with depth during 2005 both in Iida and Higashiyoka site. In April, May and June the sulphide content at Iida site shows the same trend as like 2002, 2003 i.e., gradual increasing with depth up to 0.15 m or about 0.20 m depth. After 0.20 m depth, it was decreasing gradually up to 0.40 m depth. But in July, it shows a little bit different trend, lower in the sub-surface region and gradual higher in the deeper area. But during the August, the atmospheric temperature was highest and which influence the bacterial activities more and produce much sulphide in the sub-surface layer. As a result, even in the effects of typhoon, the sulphide content is higher in the 0-0.04 m depth. The sulphide content in Higashiyoka shows the lower values than the Iida in different depths. Figure 9 shows that the sulphide content of the Iida and Higashiyoka tidal mud varied both seasonally and annually at 0.1 m depth. The sulphide content is higher at Iida site than Higashiyoka site. This is due to that Iida site is more affected by the acid treatment practice of the Porphyra sp. cultivators than the Higashiyoka site (Mochida et al., 2006). The sulphide content is much
higher level than the favorable range (0.2×10^{-3} kg kg^{-1} dry-mud) for the benthos living in the sub-surface region in the tidal mud. The sulphide content values show a great influence of the seasonal temperature. The sulphide content values show a greater value in summer and late summer and during the winter and spring the values become lower. From Fig. 9, it is also seen that the sulphide content values are gradually decreasing from 2002 to 2005, but still it is above the favorable limit for the benthos living in the mud. The decreasing trend of the sulphide content is probably due to the some sort of controlled acid treatment practice and the reduced concentration of phosphorus in the mud which is applied by the Porphyra sp. cultivators during the cultivation of Porphyra sp. Figure 10 shows that the average value of sulphide content in 0.1 m depth in summer and winter during 2002 to 2005. It is seen that the average value of sulphide content is always higher at the summer than the winter both in Iida and Higashiyokka site. In Japan the maximum variation of seasonal temperature is between summer and winter. The average value of sulphide content at summer 2002 is about 1.5×10^{-3} kg kg^{-1} dry-mud, but at the winter in that same year it reduced to 1.25×10^{-3} kg kg^{-1} dry-mud. During the 2004 summer, the average value of sulphide content is 1.11×10^{-3} kg kg^{-1} dry-mud, which is 0.4×10^{-3} kg kg^{-1} dry-mud, lower than the average value of sulphide content in summer, 2002. All the average values of sulphide content from 2002 to 2005 shows the same decreasing trend both in summer and the winter. In the winter 2005, it shows the same value of sulphide content both at Iida and Higashiyokka tidal mud. This is probably due to the gradual improvement of geo-environmental conditions at Iida site and simultaneously gradual bad condition in Higashiyokka site. Before 2002, the phosphorus content of the acid treatment agent was 8-14%. Phosphorus content was regulated to reduce less than 4% in 2002 and less than 3% in 2003 for the better geo-environmental condition in the Ariake Sea. The phosphorus is used as a feed by the bacteria and increases their activities in a suitable thermal environment and consequently increases the sulphide content in the mud (Holmer and Storkholm, 2001). From the vertical distribution of the sulphide content in the tidal mud of the Ariake sea (from 2002 to 2005) it is found that it almost follows the classical sulphide content distributions trends (Richard and Morse, 2005) i.e., smaller value in the upper region, gradually larger in the following depth and then again gradually small or about nil in the deeper region. The turbulation of the sea bed during the typhoon and great earth quake shaking are probably liable to the dissimilarity in the trend of the sulphide distribution in the various depth in the Ariake Sea tidal mud.

CONCLUSIONS

Iida site shows the higher value of sulphide content than the Higashiyokka site during 2002 to 2005. The sulphide content shows a seasonal variation both in the Iida and Higashiyokka sites. During the summer, the peak value of the sulphide content varies from 1.5 to 2.0×10^{-3} kg kg^{-1} dry-mud, since the bacterial activities and the bioturbation increase with the elevated seasonal temperature. The peak value of the sulphide content, on the other hand, is relatively low (0.5-1.0×10^{-3} kg kg^{-1} dry-mud) during the winter. The sulphide content in different depths is varied with the influence of the seasonal temperature as well as the natural disasters like typhoon in the tidal mud. With a little variation, the sulphide content distribution in vertical direction in the tidal mud show the same trend during the study period. The average sulphide content is decreasing gradually from 2002 to 2005 but still it is in the unfavorable range for the benthos which is living in the Ariake tidal mud.
REFERENCES


