INVESTIGATION ON BIOCHEMICAL ENVIRONMENTS OF SEABED IN ISAHAYA BAY

Hongyuan LI¹, Nobuhiro MATSUNAGA² and Tomohiro TAKINO³

¹Student Member of JSCE, Graduate Student, Dept. of Earth System Science and Technology, Kyushu University (6-1 Kasuga-Kouen Kasuga, Fukuoka 816-8580, Japan)

²Fellow of JSCE, Dr. Eng., Professor, Dept. of Earth System Science and Technology, Kyushu University (6-1 Kasuga-Kouen Kasuga, Fukuoka 816-8580, Japan)

³Student Member of JSCE, Graduate Student, Dept. of Earth System Science and Technology, Kyushu University (6-1 Kasuga-Kouen Kasuga, Fukuoka 816-8580, Japan)

The biochemical environments of the seabed were investigated by sampling intact sediment cores at 22 sites located in the Isahaya Bay and analyzing their sediment characteristics. The ignition loss exceeded 10 % in most of the area, and the acid volatile sulfide was also over 0.2 mg/g-dry in most of the area. A significant correlation was seen between the oxidation-reduction potential and the acid volatile sulfide. The sediment oxygen consumption velocity was very high along the north coast of the bay and along the Shimabara Peninsula in the bay mouth. The ratio of NH₄-N to PO₄-P in the pore water agreed well with the Redfield ratio under the aerobic condition, and was smaller than the Redfield ratio under the anaerobic condition. These environmental data showed that the sediment characteristics in the Isahaya Bay varied severely by location.

Key Words : Biochemical environments of seabed, sediment characteristics, pore water, Isahaya Bay

1. INTRODUCTION

The deep area of Isahaya Bay, which locates in the west-central portion of the Ariake Sea in Kyushu Island, Japan, was closed in 1997 by the reclamation dike. The reclamation area is about 35.5 km^2 and the length of the dike is 7,050 m. The water in the inner part is drained into the Isahaya Bay through the two gates at the northern and southern end of the reclamation dike.

The project was administrated by the Agriculture, Forestry and Fisheries Ministry and aimed to prevent floods in the low area and to create farmland. However, since the reclamation dike was constructed, the severe environmental deterioration such as the decline of fisheries, the enlargement of hypoxic water mass scale, the increase of the occurrence frequency of red tide has been induced and has become the social problem.

About 2,500 fishermen and residents in Fukuoka, Saga, Kumamoto and Nagasaki prefectures started a lawsuit to the Saga District Court for the government to always open two drain gates of the reclamation dike. On June 27, 2008, the ruling said that the government should keep the two gates open for at least five years, suspended for three years after the final decision would be made. Therefore, the government is pressed to conduct mid- and long-term open-gate researches and prove there is no causal relation between the reclamation project and the environmental deterioration. The government recognized the necessity of the midand long-term open-gate researches, though it appealed to Fukuoka High Court against the decision. In this social situation, the detailed environmental data of the present situation in the Isahaya Bay should be collected before conducting mid- and long-term open-gate researches in order to reveal the causal relation between the reclamation project and the environmental deterioration.

The objective in this study is to reveal systematically the spatial distributions of environmental elements of seabed in Isahaya Bay by sampling intact cores and analyzing them. As the environmental elements of seabed, the grain size, the organic matter, the oxidation-reduction potential, the acid volatile sulfide, the sediment oxygen consumption velocity and the pore water nutrients have been discussed.

2. METHODS

2.1 Intact core sampling

The Isahaya Bay is a pocket bay covering an area of about 100 km². The intact core sampling was carried out at 22 sites by hiring a professional diver. The sediment sampling sites are shown in Fig.1. Four intact cores about 15 cm high were sampled at each site using a cylindrical acrylic transparent tube with the diameter of 11 cm and the length of 50 cm. The sampled cores were kept cool in a chest filled with ice and carried to the laboratory. The core sampling was conducted at high water of spring tide or middle tide from May 7 to August 28 in 2008. Strictly speaking, we should carrv out simultaneously the core sampling at the 22 sites to show the spatial characteristics of biochemical environments of seabed. However, we did not have the equipment to keep the so many core samples in good condition and the ability to analyze them in a short period. Therefore, we were compelled to conduct the core sampling in six times. The dates when we made the core sampling at the observation sites are shown in Table 1.

2.2 Laboratory experiments

The sampled core was sliced at 0.5 cm intervals from the sediment surface to a depth of 3 cm and at 1 cm intervals from 3 cm to 10 cm. The grain size of the sliced sediment was measured using the Particle Size Analyzer (HORIBA, L-920). The ignition loss (IL) was measured after drying the samples at

 33'12'
 km
 16
 18

 0
 10
 20
 Chikugo
 11
 12
 20

 33'12'
 Kashima
 5
 7
 613
 21
 21

 33'10'
 Kashima
 1
 2
 10
 61
 20

 33'00'
 Kashima
 1
 2
 10
 61
 6

 33'00'
 Konagai
 Kashima
 7
 6
 7
 6
 13

 32'48'
 Shimabara
 Peninsula
 7
 130'12'
 130'24'
 130'36'

Fig. 1 Sampling sites of sediment cores in Isahaya Bay.

Table 1 Stations and dates of core sampling.

| Observation site | Observation date |
|-----------------------|-------------------|
| St.1, 7, 11 | May 7th. 2008 |
| St.2, 8, 12 | June 6th. 2008 |
| St.3, 9, 13 | July 7th. 2008 |
| St.4, 10, 14 | July 18th. 2008 |
| St.5, 6, 15, 16, 17 | August 21th. 2008 |
| St.18, 19, 20, 21, 22 | August 28th. 2008 |

110 °C for 2 h (ASONE, DO-450A) and then burning the organic matter in the sediment at 550 °C for 6 h (ISUZU, STR-14K). The concentrations of chlorophyll a (Chl.a) and pheophytin (Pheo.) were obtained using the standard spectrophotometric techniques after extracting the sample in 90 % acetone¹⁾. The oxidation-reduction potential (ORP) was measured by inserting directly an ORP-probe (Toko, TPX-90Si) into the sliced sediment. The acid volatile sulfide (AVS) in the dry sediment was obtained by converting the value of AVS in the wet sediment measured using a gas detector (GASTEC, GV-100S). The sliced sediment layer was centrifuged at 2000 rpm for 20 min and the extracted pore water was pretreated using 0.45 µm filters²⁾. The nutrient analysis for the filtrate was conducted using Autoanalyser an (BLTEC, SWAAT). The velocity of sediment oxygen consumption (SOC) was also obtained at each site. The detailed experimental methods for SOC velocity should be referred the paper by Li et al.³⁾

2.3 Data analysis

The results of sediment characteristics and pore water nutrients given in the Chapter 3 were averaged over surface layer (0-3 cm). The GMT



Fig. 2 Spatial distribution of Md ϕ .

(Generic Mapping Tools, Wessel and Smith 1991) was used to draw the spatial distributions of sediment characteristics, pore water nutrients and SOC velocity. The Surface Function with curvature minimization algorithm was used for interpolation.

3. RESULTS AND DISCUSSION

3.1 Grain size

The grain size is converted to the value of median diameter phi (Md ϕ). The spatial distribution of Md ϕ is shown in Fig. 2. From the range of Md ϕ from 5.6 to 6.6, we can see that silt deposits all over the bay. Considering that Md ϕ takes about 7 at the northwestern area of the Ariake Sea, these values are not sufficiently high. However, the sediment with relatively small grain size accumulates in the front of the north drain gate. As a whole, medium silt deposits from the front of the north drain gate to the off of Konagai and along the Shimabara Peninsula. On the other hand, coarse silt is observed in the wide area at the center of the bay. Medium silt deposits along the mouth of the Isahaya Bay. It







Fig. 5 Spatial distribution of ORP.

should be noted that the two-layered stratification of the grain size was observed in the intact cores sampled along the mouth of the bay and the stratification had the medium silt accumulation in the upper layer about 2 cm thick from the bed surface and fine sand deposit in the lower layer.

3.2 Organic matter

The spatial distribution of IL is shown in Fig. 3. The values of IL vary between 6.7 % and 19.8 % and exceed 10 % in most of the area. Hodoki and Murakami⁴⁾ measured the values of IL in 2002 and obtained the averaged values along the measuring lines perpendicular to the bay axis. Their values take 6.6 % at the mouth and 14.0 % at the deep area and increase toward the deep area from the bay mouth. However, our data show the large non-uniformity along the direction perpendicular to the bay axis. The region with very high values of IL is seen along the south coast. The reason may be that the construction of the reclamation dike caused outstandingly the decrease of tidal currents in that area⁵⁾ and the accumulation of a large amount of



Fig. 4 Spatial distribution of Chl.a+Pheo.



Fig. 6 Spatial distribution of AVS.

organic matter.

Fig. 4 shows the spatial distribution of Chl.a+Pheo. concentration. The values range from 7.7 μ g/g-wet to 37 μ g/g-wet. In contrast to the IL distribution, the values of Chl.a+Pheo. are higher in northwest part of the bay and lower in southwest part of the bay. The result consists with the report that red tide often observed near the north coast of the Isahaya Bay. Since no significant correlation is seen between Chl.a+Pheo. and IL, we can infer that organic matter derived from phytoplankton may not dominate over the seabed.

3.3 ORP and AVS

The spatial distributions of ORP and AVS are shown in Figs. 5 and 6, respectively. The values of ORP range between -154 mV and 174 mV. The ORP near the north drain gate and at the central part of the bay takes high positive values. On the other hand, they are negative near the south drain gate and along the mouth of the bay. Especially, in the north part of the bay mouth, the values of ORP are lower than -100 mV owing to long-term heavy organic

pollution⁶⁾.

The values of AVS in the Isahaya Bay vary between 0.04 mg/g-dry and 1.28 mg/g-dry. The AVS is higher in most of the area than 0.2 mg/g-dry, which is the standard value of water for fisheries, and the sediment environment seems to be in a serious situation. Especially, the region with the value higher than 1.0 mg/g-dry is seen near the south drain gate. Taking the IL distribution into account, we can see that the accumulation of a large amount of organic matter makes the sediment anaerobic and generates a large amount of sulfide.

Fig. 7 shows the relationship between AVS and ORP. A significant negative linear correlation is seen between the AVS and the ORP.

3.4 SOC velocity

The spatial distribution of SOC velocity, which was analyzed using the method by Li et al.³⁾, is shown in Fig. 8. The values of SOC velocity vary between 0.003 m/h and 0.017 m/h. The SOC velocity is very high in the area along the north coast and at the south part of the bay mouth. The



32°52'48 500 400 300 200 100 32°49'12

Fig. 9 Spatial distribution of NH₄-N.



Fig. 10 Spatial distribution of NO₂-N+NO₃-N.

maximum value in the north area is 0.014 m/h at St. 8 and that in the south area is 0.017 m/h at St.15. Since the area near St.8 is in the aerobic condition and contains a large amount of Chl.a+Pheo., the active organic decomposition progresses and a large amount of DO is consumed. On the other hand, the area near St. 15 is in the reducing condition and the sulfide generates there. Therefore, the high value of SOC velocity near the south area may be caused by the oxidation of the reduction substances. The values of SOC velocity are low in the central part of the bay mouth. This seems to be related to the small value of Chl.a+Pheo. included in the sediment.

3.5 Characteristics of pore water nutrients

The spatial distribution of NH_4 -N concentration is shown in Fig. 9. The values range from 126 μ M to 540 μ M and take high values near the south drain gate and St.5. It indicates that the organic matter decomposition progressed in the sulfate reduction process, as inferred from Figs. 5 and 6. The reason why the concentration of NH₄-N becomes very high near the south drain gate and St.5 is that the areas are in the anaerobic condition and the organic decomposition stops at the stage of NH_4 -N.

Fig. 10 shows the spatial distribution of NO₂-N+NO₃-N concentration. The values vary from $0.11 \ \mu M$ to $27 \ \mu M$. In contrast with the distribution of NH₄-N, the values of NO₂-N+NO₃-N are high at St.2 and St.7. In the west part of the bay, we can see that NO₂-N+NO₃-N has negative correlation with NH₄-N. Fig. 11 shows the relationship between NO₂-N+NO₃-N and ORP. The values of NO₂-N +NO₃-N are almost 0 μ M in the negative region of ORP, because in the case of ORP<0, the formation of anaerobic condition makes the reaction from NH₄-N to NO₂-N stop and the denitrification promote. In the case of ORP>0, however, NO₂-N+NO₃-N tends to increase linearly with the increase of ORP. This is due to the nitrification.

The spatial distribution of PO_4 -P concentration is shown in Fig.12. The values of PO_4 -P range from 4 μ M to 94 μ M. The values are high around St.5 and St.6 and in the north part of the bay mouth. Fig. 13 shows the relationship between PO_4 -P and NH₄-N. The open circles are used for the negative values of

130°15'36"

00 80

60

40

20



Fig. 11 Relationship between NO₂-N+NO₃-N and ORP.



Fig. 13 Relationship between PO₄-P and NH₄-N.

Fig. 12 Spatial distribution of PO₄-P.



Fig. 14 Relationship between PO₄-P and ORP.

ORP, and the filled circles for the positive values. The ratio between NH₄-N and PO₄-P agrees well with the Redfield ratio under the aerobic condition. On the other hand, the ratio is smaller than Redfield ratio under the anaerobic condition. This is due to the PO₄-P elution occurring under the anaerobic condition⁷⁾. Fig. 14 shows the relationship between PO₄-P and ORP. The values of PO₄-P are almost constant, when the values of ORP higher than 0 mV. However, the values increase with the decrease of ORP in the range where the values of ORP lower than 0 mV. This result supports the PO₄-P elution in the anaerobic condition.

4. CONCLUSIONS

In this paper, we investigated the spatial distributions of sediment characteristics, SOC velocity and pore water nutrients in the Isahaya Bay by analyzing the intact cores sampled at 22 sites.

1) The values of Md ϕ range from 5.6 to 6.6. Medium silt deposits from the front of the north drain gate to the off of Konagai and along the Shimabara Peninsula. Coarse silt is observed in the wide area at the center of the bay. The values of IL vary between 6.7 % and 19.8 % and exceed 10 % in most of the area. It means that deposit of organic matter is progressing all over the bay. Since no significant correlation is seen between Chl.a+Pheo. and IL, we can infer that organic matter derived from phytoplankton may not dominate over the seabed.

2) The values of ORP range from -154 mV to 174 mV and those of AVS vary between 0.04 mg/g-dry and 1.28 mg/g-dry. A significant negative linear correlation is seen between AVS and ORP. The AVS is higher in most of the area than the standard value of water for fisheries, and the sediment environment seems to be in a serious situation. The accumulation of a large amount of organic matter makes the sediment anaerobic and generates a large amount of sulfide near the south drain gate.

3) The SOC velocity takes very high values at two areas. One is the area along the north coast and the other is the south part of the bay mouth. In the former, as the sediment is in the aerobic condition and contains a large amount of Chl.a+Pheo., the active organic decomposition is progressing and a large amount of DO is consumed. In the latter, on the other hand, the high value of SOC velocity may be caused by the oxidation of the reduction substances.

4) The NH_4 -N takes high values near the south drain gate and St.5. The reason is that the areas are

in the anaerobic condition and the organic decomposition stops at the stage of NH_4 -N. From the distributions of NH_4 -N and NO_3 -N+ NO_2 -N, we can conduce that the denitrification has already been done near the south drain gate and St. 5, and the nitrification is progressing actively near St.2 and St.7. The values of PO_4 -P are high around St.5 and St.6 and in the north part of the bay mouth. It is due to the PO_4 -P elution under the anaerobic condition. On the other hand, the PO_4 -P concentration is low in the aerobic condition and the ratio between NH_4 -N and PO_4 -P agrees well with the Redfield ratio.

ACKNOWLEDGMENT: The study was funded by ESPEC Foundation for Global Environment Research and Technology (Charitable Trust) and Grant-in-Aid for Scientific Research (A) (PI: Prof. T. Komatsu, Kyushu Univ.) in 2008. We thank Prof. Takigawa, Kumamoto University for giving us the permission for the use of the Particle Size Analyzer (HORIBA, L-920).

REFERENCES

- Lorenzen, I.: Determination of chlorophyll and pheopigment, specctrophtometric equation, *Limnol.*, *Oceanogr.*, Vol.12, pp.343-346, 1967.
- Tokunaga, T., Soh, T., Matsunaga, N. and Kodama, M.: Investigation of seabed environments in the northern area of Ariake Sea, *Annual Journal of Hydraulic Engineering*, JSCE, Vol.49, pp.1363-1368, 2005.
- Li, H., Yamada, Y. and Matsunaga, N..: Sediment characteristics and oxygen consumption velocity of tidal flats in Ariake Sea, *Annual Journal of Hydraulic Engineering*, JSCE, Vol.53, 2009(To be published).
- Hodoki, Y. and Murakami, T.: Effects of tidal flat reclamation on sediment quality and hypoxia in Isahaya Bay, *Aquatic Conserv: Mar. Freshw. Ecosyst.*, Vol.16, pp.555-567, 2006.
- 5) Unoki, S.: Scientific and social Aspects of the problems associated with the change of tidal and tidal current in Ariake Bay, *Bulletin on coastal oceanography*, Vol.42, No.1, pp.85-94, 2004.
- Fonselius S.: Determination of hydrogen sulfide, methods of seawater analysis, 2nd edn., Verlag Chemie, Weinheim,1983.
- 7) Nobusawa, Y., Murakami, K., Kitamura, T., Koizumi, T., Kameyama, Y. and Komatsu, K.: Field observation and laboratory test for nutrient release reduction from bottom sediments with sand capping at Yokohama port, *Annual Journal of Civil Engineering in the Ocean*, JSCE, Vol.21, pp.737-742, 2005.

(Received September 30, 2008)