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BIANNUAL MONTHLY CHANGES OF SEA SLUDGE COMPOSITION FROM HIDAKA PORT, WAKAYAMA, JAPAN

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ABSTRACT: The composition of sea sludge varies from location to location and from time to time, since it is affected by various external environmental factors. In this study, we analyzed the organic and inorganic contents of sludge samples collected for two years (25 months) from the Hidaka Port in Wakayama. Weight-loss analyses for 25 months indicates that the highest inorganic content was in July 2016 (99.11%), and the lowest in April 2018 (87.46%). We then conducted EDX Spectrometry analyses on some samples, focused on Si, Al, Fe, and S, for the samples of the first 16 months. Our result indicated that while the dynamics of total inorganic content was naturally synchronized inversely with that of the organic content, it was not completely reflected in the dynamics of individual inorganic elements. For example, Fe and Al changes were not congruent with the changes of the total organic and inorganic contents. However, Si and S showed possible agreements with the changes of total inorganic and organic contents. From these results, we deduced that the dynamics were probably caused by environmental factors such as weather and water temperature, and the activities of living organisms such as diatoms, alga, and microbes.

Keywords: Sea sludge, Inorganic matter, Time series dynamics, Water temperature, Geochemistry

1. INTRODUCTION

Sedimental sea sludge is formed through the deposition of organic and inorganic matter brought in to the sea by river, rain, and sea currents, resulting in viscous mud-like sediment piling on the seafloor, with a distinct bad smell and dark color caused by its sulfide compounds [1]. Information on the chemical composition dynamics of sea sludge will help us to understand not only the interactions among the different factors involved in sea sludge formation, but also about the interactions among the organisms living in and on the sea sludge. Meanwhile, the information might also bring insights about the effects of human activities on seafloor environment.

The inter-relationships and interactions among climate and weather dynamics and other external environmental changes, and the dynamics of chemical compositions of the sea sludge, are rarely studied. Several studies reported the compositional aspect of sea sludge samples collected from single sampling localities. For example, we have reported the chemical compositions of samples from the Funabashi Port in Chiba as 23.61% [2], and the Hidaka Port in Wakayama as 7.27% [3]. Although lacking detailed information, insights from such studies have allowed for the formulation of a generalized definition of the sea sludge [1]. However, since sea sludge composition itself is influenced greatly by small differences in the environment of the location, to do an objective and standardized comparison of sludge collected from different locations is difficult [1,4].

To our knowledge, there was no report about sea sludge content changes collected in a time series from one particular sampling point, until our previous study reporting changes of the organic content in time-series samples collected from Hidaka Port in the Gobo coastal area [1]. The result of that study indicates that environmental data such as weather condition and water temperature might explain such dynamics, while possible influence of anthropogenic and microbial activities to such dynamics were also discussed.

In this study, we focused on the changes of inorganic content over time on samples collected from Hidaka Port for two years (25 months). We collected additional sludge samples for 12 months (August 2017 – July 2018) and conducted compositional analyses to assess changes in both organic and inorganic matters. Next, we analyzed the inorganic contents of the samples collected for 13 months (July 2016 – June 2017). The result of the samples' organic content analysis was reported in our previous paper [1]. Obtained results were then combined and discussed together in order to obtain a bigger picture of the interactions between environmental factors, and possible biological factors.

2. MATERIALS AND METHODS

2.1 Sea Sludge Sampling

Wet sea sludge from Hidaka Port in Gobo City (33°52'55.3"N, 135°09'10.7"E) in Wakayama Prefecture was collected manually. Details about sampling and fresh sample treatment methods were described in our previous study [1]. Samples were collected once a month for 12 months from August 2017 to July 2018 from one sampling location at three different loci. The sludge from the three loci were mixed evenly prior to further analyses, in order to avoid compositional bias.

2.2 Analyses of Ratio in Total Organic Contents and Total Inorganic Contents

Thermo-Gravimetric (TG) analyses were conducted on oven-dried samples in order to obtain the information of organic content. TG analyses were conducted in three conditions: (1) the original dried sludge sample, (2) dried-up sample further burnt at 100ºC in order to obtain information about both inorganic and organic contents, and (3) dried sample burnt twice, first at 100ºC and later at 600ºC, to get rid of the organic matter completely. The mass lost after burning can be considered as the total mass of organic content.

Inorganic content of a sample was inferred by calculating the mass left after burning at 100ºC and 600ºC, considering sample (1) (the solid/dried soil sample) as the standard.

The total organic contents and total inorganic contents analyses were conducted on all samples collected for 2 years.

2.3 Main Elements Analyses Using EDX

We measured silicon (Si), aluminum (Al), iron (Fe), and Sulfur (S) in surface of sludge using the Energy Dispersive X-ray spectrometry (EDX) (SEM-EDX; Miniscope TM-3000; Hitachi Ltd.). Sample preparations were as follow: First, wet sludge samples were dried in an oven at 100ºC for 10–15 minutes. Dried sample clumps were then crushed to turn them into coarse powder. The powder was mounted on carbon stage using carbon tapes, were analyzed using the SEM-EDX. From the analysis, values in percentage showing proportions of the four elements analyzed relative to one another were obtained. For each sludge sample, three mounted powder samples were prepared and analyzed in order to avoid sampling bias.

2.4 Sample and Data Availabilities

In our previous study, we only analyzed the organic content of samples collected in July 2016 to July 2017 [1]. In this study, we analyzed specific inorganic elements (Si, Al, Fe, and S) for those samples, except for the ones from August and October 2016, because of insufficient amount of samples collected from those two months. Meanwhile, while we were able to analyze both the organic and inorganic contents of samples from August 2017 to July 2018 (12 months), we only analyzed the composition of the specific inorganic elements for the months between July 2016 to October 2017. Therefore, in this study, we are reporting the compositional ratios of Si, Al, Fe, S only for 14 months. However, we believe these data is already enough and solid, if discussed totally with other data such as the organic matter changes.

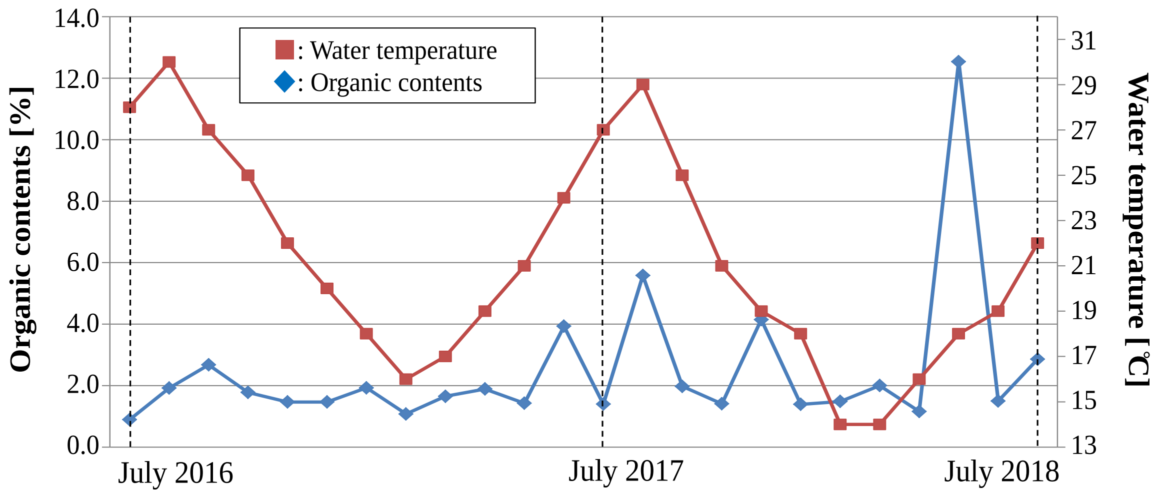

Fig.1 Analysis of total organic content and water temperature

3. ENVIRONMENTAL DATA

Weather condition and rainfall precipitation data of the three consecutive days before and on the day of sludge collections were collected from the homepage of the Japan Weather Association (http://tenki.jp/) and from the homepage of the Japan Meteorological Agency (http://www.data.jma.go.jp/obd/stats/etrn/index.php), respectively. Information of seawater mean temperature for the week of the sampling date was obtained from the homepage of the 5th Regional Coast Guard Headquarters (https://www1.kaiho.mlit.go.jp/KANKYO/KAIYO/qboc/backnumber.html).

4. RESULTS

4.1 Additional Analysis of Total Organic Content

4.1.1 The dynamics of total organic content

We have reported the dynamics of organic content in a set of time-series sludge samples collected for a year previously, from July 2016 to July 2017 [1]. In this study, we added the results obtained from more samples collected from the same sites in Gobo/Hidaka coast, for another 13 months (from July 2017 to July 2018), totaling in a series of samples showing monthly organic contents for two years (25 months). When we reconsidered our results (Fig.1) to include the values for the 25 months, we saw a possible cyclical pattern of the organic content changes. The highest organic content was 12.54% in April 2018 (different from our previous study [1] = in June 2017, 3.93%), while the lowest value was 0.89% in July (similar to our previous study [1]).

4.1.2 Weather condition and weather temperature

The highest water temperature was observed during the sampling week of August in 2016 and 2017, after gradually increasing, and then gradually decreasing in other months. Interestingly, when the trends of organic content dynamics vs. water temperature changes during the months of July to October in 2016 vs. 2017 were compared, we observed that organic content decrease happened simultaneously with the gradual decrease of water temperature. Our data indicated that the organic content in 2016 started to decrease about a month after water temperature decrease, while in 2017 the decrease started in the same month.

We also observed a possible relationship between weather condition and the changes in organic content, in agreement with our discussion given in our previous report [1]. Weather patterns in the months of August and September 2016, and June of both year and August of 2017, heavy rains fell 1–3 days before the sampling date of each month. In these summer months, weather conditions around the sampling dates were similar. Interestingly, organic contents of the sea sludge samples from these months were observed to be relatively high. This observation is also in agreement with water temperature changes mentioned previously.

4.2 Analysis of Inorganic Content

4.2.1 The dynamics of total inorganic content

The dynamics of the total inorganic content of the time series samples correlate inversely with those of the total organic content. We found that the sea sludge collected from Hidaka Port is composed mainly of inorganic materials (mean percentage for 2 years = 97.35%). The maximum value of the total organic content was 99.11% in July 2016, while the minimum value was 87.46% in April 2018.

4.2.2 SEM-EDX Results of the four major elements (Si, Al, Fe, S)

We conducted SEM-EDX analyses to identify the compositional changes of the four main inorganic elements: Si, Al, Fe, and S (Fig.2). The average value of Si for all samples collected for 16 months is 67.47% (maximum value: 69.18%,

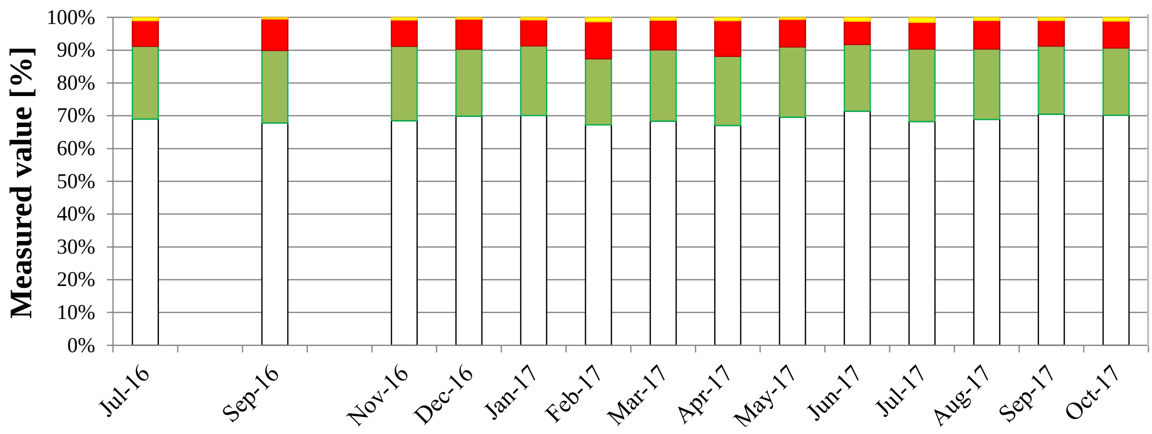

Fig.2 Analysis of total inorganic content; from bottom: Si, Al, Fe and S

October 2017; minimum value: 62.82%, August 2017). The values for all months besides the maximum and minimum values are all more than 60%. When the low organic content mentioned previously (average value: 2.24%) is also considered along with the high Si content, it can be said that the sludge from Hidaka Port is very close to sand.

The average value of Al is 20.82% (maximum value: 22.33%, November 2016; minimum value: 19.59%, June 2017). Fe and S are the elements thought to affect the colorations and smell of sea floor sedimental sludge and mud. EDX analyses of our samples showed the average value of Fe to be 8.52% (maximum value: 11.19%, February 2017; minimum value: 6.73%, June 2017). The average value of S is 0.90% (maximum value: 1.45%, July 2017; minimum value: 0.49%, November 2016). This composition could explain the gray color and slight rotten-egg smell of the sludge from Hidaka Port.

While random dynamic changes of compositional ration of Fe in the samples were seen, only slight changes of S were observed. Because the changes of S are very small (Fig.3), we conducted log approximation. We obtained the formula below to express our results:

$$Y = 0.286 + 0.298\ln(x) \quad (1)$$

The result (Fig.4) showed that although the changes of S across the whole observation period are very low, a cyclical change could still be seen, especially if we compared the results of similar months from differing years the change. The changes in both S (Fig.3) apparently are synchronized inversely with changes of the organic contents.

5. DISCUSSIONS

5.1 Possible External Factors Affecting the Organic Matter Composition Dynamics of The Seafloor Sludge from Hidaka Port

Previously, we suggested that the change in the organic matter content in the sea sludge from Hidaka Port was probably caused by environmental factors such as water temperature and weather conditions, and biological factors such as living organism activities and life cycles [1].

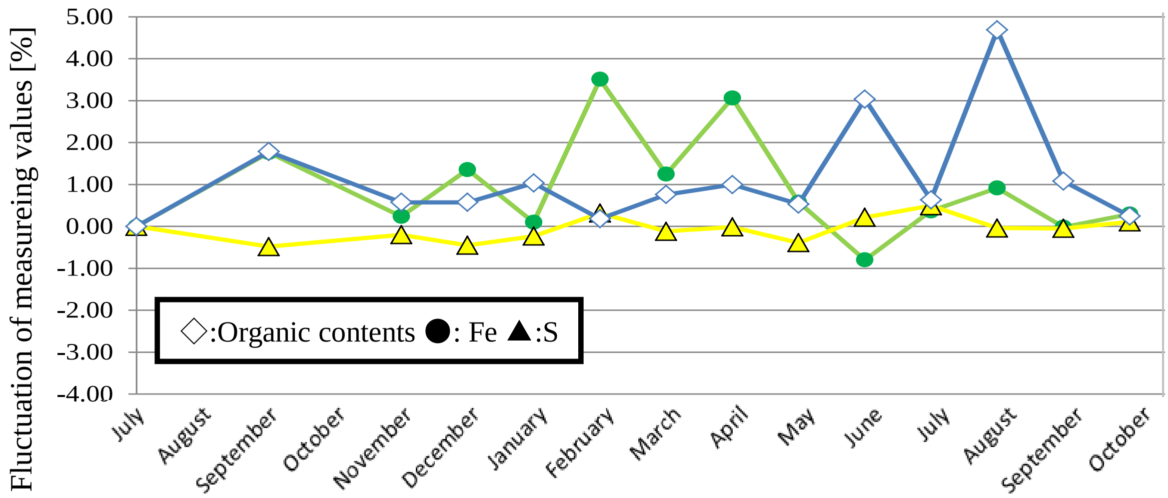

Fig.3 Comparisons of the organic contents, Fe, and S

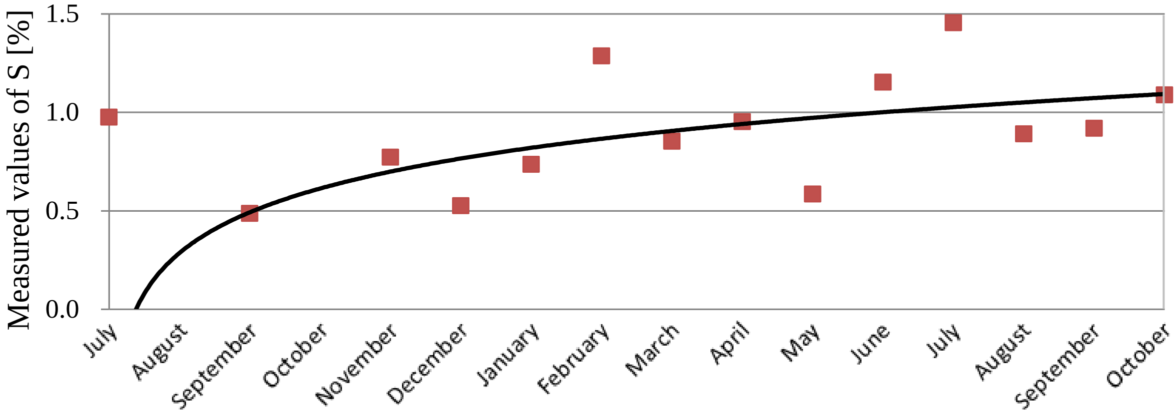

Fig.4 Log approximation in analysis of S

In our present study, we conducted additional analyses on samples taken in the months of August 2017 to July 2018, making the total samples to be 25 months. The addition of the measurement results of the organic content has made comparisons among the corresponding months of 2016, 2017, and 2018, possible. The comparisons indicated a congruency of fluctuations between the corresponding months of 2016, 2017, and 2018 (July, August, September, and October) for which data are available. The data showed that in those two years, a decrease in the organic content rate was observed a month after the water temperature peaked in 2016, whereas in 2017 the organic matter decrease happened with the samples collected at the end of the month when the water temperature peaked (Fig.1). This probably suggests that during the hot months of summer, the warm water temperature might have caused microbe proliferations [5], which might then cause an increase in organic matter deposition. Meanwhile, a decrease in organic matter composition of the sludge samples collected when water temperature dropped at the end of summer might probably be explained in two ways. While warm temperature of water might cause an increase in microbial activities, temperature decrease might have caused microbial activities to also decrease. The decrease in organic content could be caused by it. Besides that, warm water is known to leach organic matter [6]. During summer months, increased microbial activities might replenish the leached out organic matter in the sedimental sludge. However, when microbe activities decrease, the replenishing pace might not be able to catch up with the leaching pace, hence the roughly a month time lag of the decrease of organic content. In our previous report [1], we also discussed possible contributions of the presence and absence of vegetation growths such as seaweeds and mosses (Fig.5 A and B) caused by its life cycle [7,8]. In this study, we found that our hypothesis about a possible correlation among microbial activities, water temperature, and seaweed life cycle, was not rejected. We observed that rain fell several days prior to the sampling dates. This might have contributed to the increase of organic content, which was probably caused by leached inland organic matter brought in to the sea by the river (Fig.5. C and D). However, while we found no contradiction with what we proposed in our previous paper [1], at present, we are unable to decisively pinpoint any strong correlation between rainfall and the dynamics of organic content. Accordingly, further studies to specifically see if rainfalls affect compositional changes of the sedimental sea sludge must be conducted.

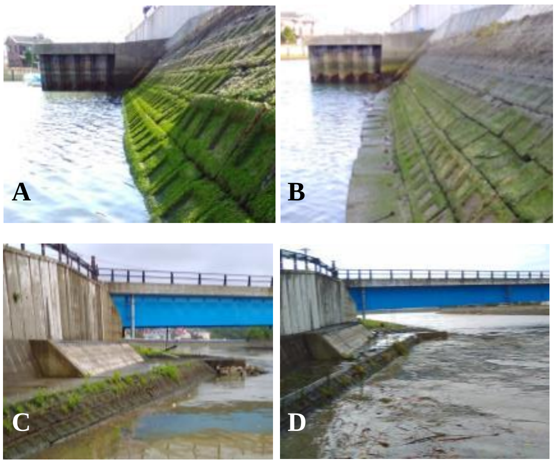

Fig.5: The dynamics of biological and weather conditions of Hidaka Port. Seaweed and moss growth in February 2017 (A), and in February 2018 (B). Drought (July 2017) (C) and heavy rains (September 2018) (D) affecting the amount of water, and thus most likely also the condition of the bottom sediments of Hidaka Port.

5.2 Possible External Factors Affecting the Organic Matter Composition Dynamics of the Seafloor Sludge from Hidaka Port

In order to investigate the factors of change in the main components of inorganic matter, we conducted EDX analyses using the Scanning Electron Microscope (SEM) on the time-series sludge samples on the four main elements known as the main components of sea sludge: we compared fluctuation in organic matter and Si, Al, Fe, and S. We surprisingly found out that Fe fluctuations are uncorrelated with any content changes. Therefore, at least in this study, we are unable to connect the irregular fluctuations of Fe during the whole sampling period with changes in organic components, or environmental factors. Meanwhile for S, we found a possible cyclical dynamics inversely correlated with the organic contents. This is probably related to sulphate-producing aerobic microbial activities. Further studies must be conducted to pinpoint the possible causes such as anthropogenic, biological, or environmental factors, and the mechanism. We also noted that the average percentage of S of the Hidaka Port samples is very low (0.90%), when compared to samples collected from the Funabashi Port in Chiba (10.29% [3]). A study of sludge collected from the Funabashi Port in Chiba [9] showed that the amount of dissolved oxygen (DO) is higher in sludge with lower content of sulfide. Therefore, the low S in Hidaka Port sludge might indicate high DO. Further studies, however, will be needed to confirm this suggestion.

In our present study, the changes of Si across time were found to be highly dynamic (Fig.6). When we looked at our non-EDX SEM data, we found traces of the phytoplankton diatoms (Fig.7) from the sludge sample of the month October 2017, which is the time when we observed an increase in Si percentage (Fig.6). Diatoms are classified as a type of algae, members of the superphylum Heterokonta. One oftheir main characteristics, besides their ability to photosynthesize, is their dense and heavy cell wall made of silica (SiO_2), which is also the cause of their non-motility. Because they are non-motile, they depend on water flow and turbulence to stay suspended in water with enough sunlight, and sink to the bottom of the sea when no external force keeping them afloat [10]. As a phytoplankton, their life cycle depends on water temperature and the availability of sunlight [10,11].

A previous study focused on the abundance of diatoms collected from various depths in the Nada-Kumano coastal area, which is adjacent to our sludge-sampling location [12]. The study reported that diatoms from the area at the depth of 200 m are abundant during the months of April, August, and at the depth of 1000 m in October. This observation result sits very well with our results, which showed that Si percentage is high during the months of September 2016, May 2017, and August 2017 (Fig.6), which means that high Si contents were observed on the month, or a month after diatoms high abundance was reported at the depth of 200 m. Takeuchi had reported the presence of an upwelling current from the bottom to the surface in the sea of the area [13]. Ishikawa et al also suggested that this upwelling could explain the abundance at different depths on different times, similar to previous studies in other areas [12,14,15]. Our samples were collected from shallow/surface waters (ca. 30 cm depth) at the Hidaka Port. Taking everything into account, a possible explanation of the relationship between the abundance of diatoms and high Si contents can thus be conceived. Probably, the upwelling brought many of the diatoms to the surface water level. Later, since the diatoms are non-motile, they settled down on the seafloor sludge close to the surface, contributing to the high Si content of the sludge. The one-month time lag between the abundance of diatoms at 200 m depth reported by Ishikawa et al [12] and peaks of Si content in the samples could be explained as the time the diatoms needed to move up from the depth of 200 m to the surface, and then to settle down on the shallow seafloor sludge.

We also found that in our data, Si changes and fluctuations were in agreement with those of the total organic content (Fig.6), indicating a possible connection. However, further studies to pinpoint the underlying connection are needed. When based on our present result only, however, we might hypothesize that changes in total organic content might be affected by the changes of Si content in the sludge, which most likely is caused by the abundance of diatoms in shallow water. This relationship might also explain the inverse relationship between Si and organic content.

6. CONCLUSION

By adding data for eight additional months, we were able to confirm our hypothesis conceived from our observation in the previous study [1]. Our result is summarized below:

(1) The direct influence of water temperature and weather condition could involve warm-water leaching of organic content, and organic materials from inland areas brought in by rain and river flow.
(2) Indirect influence might be related to the presence of microbes and other biological agents such as seaweed and diatoms, which life cycles and biological activities probably depends on water temperature and weather.
(3) Inorganic analysis result indicates that Fe changes were probably random and thus

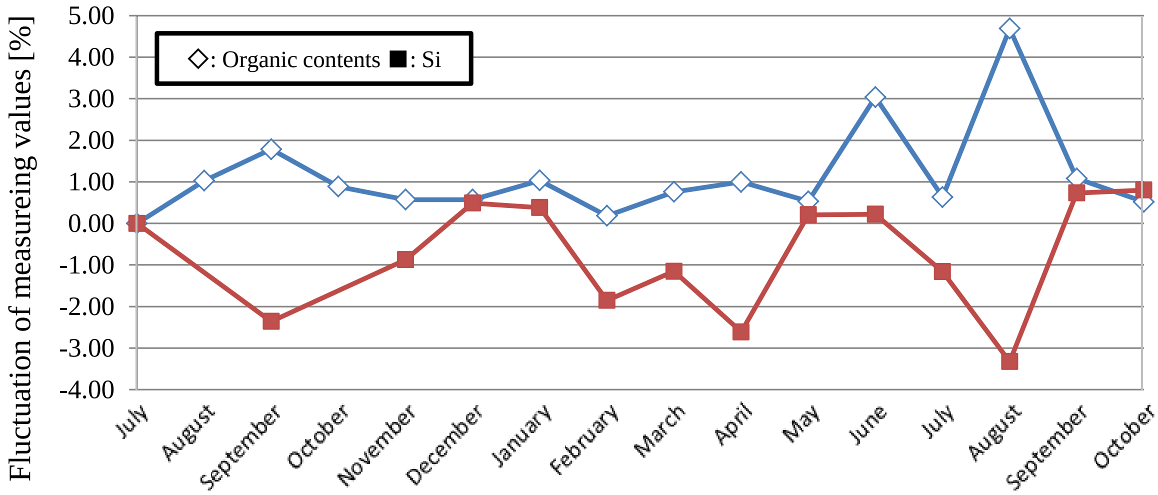

Fig.6: Comparison with organic content and Si

inexplicable with our present result. Meanwhile, S changes were most likely cyclical over time, and further studies are still needed to clarify the causes of this dynamics.

(4) Si changes are probably connected to the presence and/or abundance of diatoms. Al changes were seemingly synchronized with those of Si across time, causing the ratio of Si to Al to be stable at 3-1.

(5) We cannot rule out causes of anthropogenic origin, such as farming, contributing to the dynamic changes of sea sludge compositions.

We plan to continue our study across a longer time span, in order to further confirm the presence or absence of a cyclical pattern. More studies are needed to pinpoint the exact actual causes of organic content changes, most likely by using other methods including those of microbiology and molecular genetics, such as flow cytometry and eDNA. Similar biological methods can also be used to pinpoint the changes in Si content. Other studies to closely monitor the effects of rain and water temperature, and inputs from terrestrial waters (e.g. rivers) must also be conducted in the future.

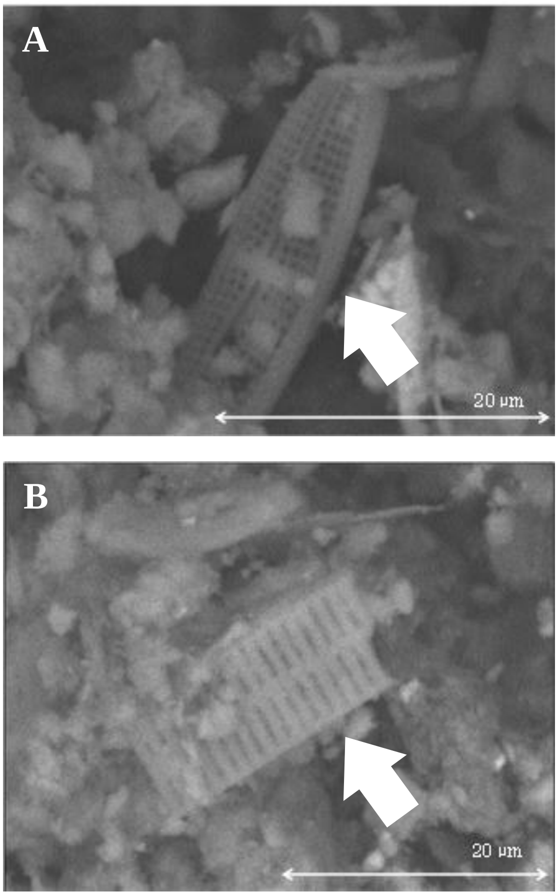

Fig.7 Phytoplankton diatoms in sludge samples.

7. ACKNOWLEDGMENTS

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