COMPOSITIONAL CHANGES IN SEA SLUDGE SAMPLES FROM HIDA K PORT IN WAKAYAMA, SOUTHWEST JAPAN, COLLECTED MONTHLY FOR A PERIOD OF 16 MONTHS

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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 16 months from the Hidaka Port in Wakayama. Weight-loss analyses for 16 months indicates that the highest inorganic content was in July 2016 (99.11%), and the lowest in June 2017 (94.42%). We then conducted EDX Spectrometry analyses on the samples, focused on Si, Al, Fe, and S. Our result indicated that while the dynamics of total inorganic content is naturally synchronized inversely with that of the organic content, it is not completely reflected in the dynamics of individual inorganic elements. For example, S is relatively stable throughout the year, and Fe changes are not congruent with the changes of the total organic and inorganic contents. However, Al and Si show a possible agreement 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

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. Because of the organic material and sulfide compounds, sea sludge has a dark color and bad smell [1]. Information on the chemical compositions of sea sludge is important, since such information will help us to understand the interaction between different environments related to the formation of the sedimental sea sludge, but also about the interactions between the organisms living in the sea sludge as the matrix of their habitats. Such information might also bring insights about the effects of human activities on seafloor environment. However, 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 environs 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 16 months (samples collected
for 12 months analyzed in our previous paper plus additional samples collected in the following 4 months), from July 2016 to October 2017, besides also revisited and reanalyzed the organic content dynamics data from our previous study [1].

MATERIALS AND METHODS

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 method and post-sampling oven treatments followed our previous study [1]. Sea sludge samples were collected once a month for 16 months from July 2016 to October 2017 from one sampling location at three different loci. The sludge from the three loci were mixed together for further analyses, in order to avoid compositional bias.

2. Analysis of total organic and 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 and total inorganic contents analyses were conducted on all samples collected for 16 months.

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 were 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.

We were unable to do EDX analyses for August and October, 2016, because of insufficient amount of samples for those two months. Therefore, we obtained only the information of total organic and inorganic contents for those two months.

4. 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.dia.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 (http://www1.kaiho.mlit.go.jp/KANS/).

RESULTS

1. Additional analysis of total organic content

a) 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 three months (August–October, 2017), totaling in a series of samples showing monthly organic contents for 16 months. When we reconsidered our results to include the values for the whole 16 months, we saw a possible cyclical pattern of the organic content changes. The highest organic content was 8.82% in August 2017 (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]).

b) 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
decline 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
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.

2. Analysis of inorganic content

a) 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
16 months = 97.96%). The maximum value of the
total organic content was 99.11% in July 2016,
while the minimum value was 91.18% in August
2017.

b) 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 of a sea sludge: Si, Al, Fe, and S. The
average value of Si for all samples collected for 16
months is 67.47% (maximum value: 69.18%,
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.
Meanwhile, the average value of Al is 20.82%
(maximum value: 22.33%, November 2016;
minimum value: 19.59%, June 2017). This makes
the composition of Si to be three times of Al (Si : Al
≈ 3 : 1). This compositional ratio is very close to
the materials of cement such as blast-furnace slag
[5] and fly ash [6].

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). Meanwhile, 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
croton-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, in order to confirm the
stability of S, we conducted log approximation. We
obtained the formula below to express our results:

\[ Y = 0.286 + 0.298 \ln(x) \]  

(1)

The result (Fig 1) showed that the changes of S
across the whole observation period are very low,
which means that for the whole 16 months, the
composition of S is relatively stable.

4. DISCUSSIONS

1. Possible external factors affecting the organic
matter composition dynamics of the seafloor
sludge from Hidaka Port

In a previous study, 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].

In our present study, we conducted additional
analyses on samples taken in the months of July to
October 2017, making the total samples to be 16
months. The addition of the measurement results of
the organic content has made comparisons among
the corresponding months of 2016 and 2017,
possible. The comparisons indicated a congruency of
fluctuations between the corresponding months of
2016 and 2017 (July, August, September and
October) for which data are available. The data
showed that in both 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 [7], 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 [8]. 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 one 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 seaweed (a and b in Fig. 2, as change by season, in Hidaka port) caused by its life cycle [9] [10].

In this study, we found that our hypothesis about a possible correlation among microbial activities, water temperature, and seaweed life cycle, is 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. However, while we found no contradiction with what we proposed in our previous paper [1], we are unable to decisively pinpoint any strong correlation between rainfall and the dynamics of organic content. Accordingly, further studies to specifically see if rain affects compositional changes of sea sludge must be conducted in the future.

2. Possible external factors affecting the inorganic 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 (Fig. 3), Al (Fig. 4), Fe (Fig. 5), and S (Fig. 6). We surprisingly found out that S is stable throughout the year, and Fe fluctuations are uncorrelated with any content changes. Therefore, at least in this study, we are unable to connect the stability of S and the irregular fluctuations of Fe during the whole sampling period with changes in organic components, or environmental factors. 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 [11] 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 dynamics. When we looked at our non-EDX SEM data, we found traces of the phytoplankton diatoms (Fig. 7 a, b) from the sludge sample of the month October 2017, which is the time when we observed an increase in Si percentage (Fig. 5). Diatoms are classified as a type of algae, members of the superphylum Heterokonta. One of their main characteristics, besides their ability to photosynthesize, is their dense and heavy cell wall made of silica (SiO₃), 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 keep them afloat [12]. As phytoplankton, their life cycle depends on water temperature and the availability of sunlight [12] [13].

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 [14]. 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. 5), 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 [15]. 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 [14] [16] [17]. 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 [14] 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. 3), 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 the amount of organic content (Fig. 3).

Al content fluctuations were found to be congruent to Si. Although we are unable to pinpoint a possible cause, this "synchronized" dynamics of Al to Si have caused the proportion of Si : Al to be relatively stable at 3 : 1. This also makes that both Si and Al changes are in agreement with the dynamics of total inorganic content of the sludge samples across the whole 16 months (Fig. 3, Fig. 4). Future studies will be needed to elucidate the reasons and mechanisms behind the changes and maintenance of the Si : Al proportion.

CONCLUSION

By adding data for three additional months, we were able to confirm our hypothesis conceived from our observation in the previous study [1]. That is, (1) the dynamics of the organic contents over time are probably directly and indirectly affected by external environmental factors such as water temperature, and weather condition. (2) The direct influence of water temperature and weather condition could involve warm-water leaching of organic content, (3) and organic materials from inland areas brought in by rain and river flow. (4) 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. We also cannot rule out causes of anthropogenic origin, such as farming, contributing to the dynamic changes of sea sludge compositions.

We also concentrated on changes of percentage of some elements composing the inorganic content of sea sludge. Our result indicates that S content did not fluctuate over time, and Fe changes were...
probably random and thus inexplicable with our present result. Meanwhile, Si changes are probably connected to the presence/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 to 1. However, we were unable to pinpoint what exactly the cause of the dynamics of Al in the sludge samples.

We plan to continue our study in order to obtain more information across longer time span, in order to confirm the presence or absence of a cyclical pattern. More studies are needed to pinpoint the exact actual cause 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 must also be conducted in the future.

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