Dynamic changes of organic content over time in the sea sludge collected from the Gobo/Hidaka coastal area in Wakayama, southwest Japan

H Hirano1*, D Semura1, K Sakamoto1, T Toyama2, DHE Setiamarga3*

1Department of Civil Engineering and Urban Planning, National Institute of Technology, Wakayama College, Gobo City, Wakayama, Japan 644-0023
2Department of Materials and Applied Chemistry, College of Science and Engineering, Nihon University, Tokyo, Japan 101-8308
3Department of Applied Chemistry and Biochemistry, National Institute of Technology, Wakayama College, Gobo City, Wakayama, Japan 644-0023

*E-mail: hirano@wakayama-nct.ac.jp; davin@wakayama-nct.ac.jp

Abstract. The Gobo/Hidaka coastal area is known for its pristine nature and biodiversity, but recent urban developments might have affected its environmental condition. In previous study, we found a relatively low amount of organic matter from the Hidaka Port samples. In this study, we determine the possible cause of such an anomalous low organic matter content. Sludge samples were collected from the bottom of the sea of Hidaka Port monthly for one year (July 2016 to June 2017). The result showed the lowest content of organic matter in July 2016 (0.89%) and almost repeated in November 2016 (1.47%), February 2017 (1.08%), and May 2017 (1.42%). Meanwhile, the highest record was in June 2017 (3.93%). The fluctuating organic contents are in congruent with the water temperature data. The possible interactions among the seawater temperature, monthly rainfall amount of the corresponding months, possible abundance of marine microbes, and farming in the surrounding area might have caused the fluctuations. Our result would certainly be useful to infer the interrelationships of anthropogenic activities and other biotic and abiotic factors to the sea sludge, and eventually, the oceanic environment. Future studies needed to analyze inorganic content and data collections over multiple years.

1. Introduction

Sedimentary sea sludge is an important component of the seafloor environment. For example, it plays an important role as one of the matrices for living organism habitats. Therefore, information on the chemical compositions of sea sludge (e.g. the organic and inorganic contents) and their dynamics might bring an understanding about the interaction between environments and organisms living in the matrix. Furthermore, such data might bring possible insights about the effect of anthropogenic influences on seafloor environment.

Sea sludge is formed through the deposition of organic and inorganic matter at the seafloor, causing viscous mud-like sediment to pile at the bottom of the sea. By definition, sea sludge is different from a mud because of the lack of organic matter and sulfate in the latter. However, it is very difficult to differentiate the two seafloor sediments simply through its outer appearance. In Japan, sea sludge is always associated with bad smell, causing it to be called “hédoro” (flatulence (= hé); and mud (= doro)) or “hénatsuchi” (a wet darkly mud). Because of this compositional difference the organisms inhabiting mud and sea sludge are presumably different.

Some previous research has studied the chemical characteristics of the sea sludge [5, 6]. However, such studies have concentrated only on elucidating the compositional aspect of the sea sludge. Moreover,
the sea sludge used as the objects of those studies were collected from different sampling localities, and located at different times. Since sea sludge composition is influenced greatly by small difference in the environs of the location, an objective, standardized comparison of the studies difficult [1]. In our previous study, we reported that samples collected from different coastal areas in Japan (Funabashi-port in Chiba vs. Hidaka-port in Wakayama) showed different compositional values in organic and inorganic contents, and thus in their characteristics (table 1) [4, 6]. The generalization of the results obtained from such studies, however, have allowed for a standard-but-vague definition of a sea sludge based on its chemical composition. The definition of sea sludge can thus be given as follow: Mud-like viscous sedimentary substance composed of (1) organic matter partially derived from the activities and carcasses of living organisms including microorganisms, (2) inorganic matter derived from the deposition of mud, silt, and sand, and (3) high sulfur content (which gives the sea sludge its distinct "rotten egg-like smell" and dark color).

The lack of a more specific definition has caused a detailed classification of seafloor sludge non-existent. Such lack of a classification system based on the differences and dynamic changes in compositions of the different types of sludge, and their relations to differences and changes of the environments, have hindered a detailed understanding of the position and importance of sludge in seafloor environment. Meanwhile, the inter-relationships and interactions among natural ecosystem changes, climate and weather dynamics, biological activities, and other external environmental changes, with the dynamic chemical compositions changes of the sea sludge, are rarely studies. In fact, to our knowledge, there is no report about sea sludge compositional changes collected in a time series from one particular sampling point.

In this paper, we report the changes of organic content of the coastal sea sludge in natural conditions collected from a single location at the Hidaka Port in Gobo/Hidaka coastal area in the Kichuu region of the Wakayama Prefecture, southwest Japan (figure 1). The Gobo/Hidaka coastal area is known for its pristine nature and biodiversity, but recent urban developments might have affected its environmental condition. In order to obtain an insight on the dynamic changes of the organic content of the sea sludge collected from one particular location, we collected sea sludge samples in a time-series for 13 months. We also surveyed and collected relevant local weather and water temperatures in order to infer possible correlations among the three data sets. We concentrated on the changes in organic content because it is relatively easy to detect and analyze with relative accuracy. Moreover, since changes in organic content are usually influenced by external environmental factors such as living organism activities including microbes and humans, the data might enable us to discuss about the possible dynamics of such external factors.

| Collecting sites          | Measured days | Organic contents [%] |
|--------------------------|---------------|---------------------|
| Chiba (Funabashi Port)   | 15/9/2011     | 23.6                |
| Wakamaya (Hidaka Port)   | 15/6/2015     | 7.3                 |
2. Materials and Methods

2.1. Sea sludge sampling and weekly water temperature data
Wet sea sludge from Hidaka Port in Gobo City in Wakayama Prefecture (figure 1) was collected manually. The sea sludge was obtained from its natural environment. To see the dynamic changes of the organic content of the sludge from one geographic locus, we collected sea sludge samples once a month for 13 months from July 2016 to July 2017. Samples were collected from one sampling location at three different loci, and the sludge from the three loci were mixed together for further analyses, in order to avoid compositional bias. Sampling dates for each month are shown in table 2, along with the information of the mean temperature of water for the week of the sampling date. Seawater temperature data of the week of the sampling dates, of Wakayama region, were also referenced from the homepage of the 5th Regional Coast Guard Headquarters (http://www1.kaiho.mlit.go.jp/KAN5/).

Then, the wet sea sludge samples were oven-dried, in 100 °C for 10-15 min to evaporate the moisture content. Afterward, one gram of the dried sample was extracted for future analyses.

Table 2. Sample sludge collection dates and corresponding weekly water temperature.

| Collected days     | Water temperature [°C] | Collected days     | Water temperature [°C] |
|--------------------|------------------------|--------------------|------------------------|
| 7 July 2016        | 28         | 26 February 2017   | 16         |
| 8 August 2016      | 30         | 29 March 2017      | 17         |
| 27 September 2016  | 27         | 25 April 2017      | 19         |
| 31 October 2016    | 25         | 24 May 2017        | 21         |
| 29 November 2016   | 22         | 28 June 2017       | 24         |
| 22 December 2016   | 20         | 25 July 2017       | 27         |
| 25 January 2017    | 18         |                     |            |

2.2. Analysis of organic content
We conducted Thermo-Gravimetric (TG) analysis [6] on the oven-dried samples to obtain the information of organic content, in three conditions: (1) the original dried sludge sample, (2) dried-up
sample further burnt at 100 ºC in order to obtain information about both inorganic and organic contents, and (3) dried sample burnt twice, first at 100 ºC and later at 600 ºC, to get rid of the organic matter completely. The organic content of samples was then deduced by calculating the lost mass caused by burning at 100 ºC and 600 ºC, considering sample (1) (the solid/dried soil sample) as the standard.

2.3. Weather condition data
We collected weather data of three consecutive days before, three consecutive days after, and on the day of sludge collection, provided by the Japan Weather Association (http://tenki.jp/).

3. Results

3.1. Analysis of organic content
Heat weight loss analyses (TG analysis) on the samples with burning temperature between 100 ºC to 600 ºC indicate a fluctuation of the content of organic matters in the sludge samples over time in the course of one year. Our observation suggested that the fluctuations are random but not drastic, with the "usual" organic content in a given month as around 1.00% to 2.00% (Table 3). The lowest content in July 2016 (0.89%) and was almost repeated in November 2016 (1.47%), February 2017 (1.08%), and May 2017 (1.42%). However, data of some of the months show drastic fluctuations of organic content. The value in June 2017 was 3.93%, and in September 2016 was 2.68%, which were twice than the "usual" value of 1 - 2%.

| Collected days | Organic contents [％] |
|----------------|----------------------|
| 2016 July      | 0.89                 |
| August         | 1.92                 |
| September      | 2.68                 |
| October        | 1.78                 |
| November       | 1.47                 |
| December       | 1.47                 |
| 2017 January   | 1.93                 |
| February       | 1.08                 |
| March          | 1.65                 |
| April          | 1.89                 |
| Mei            | 1.42                 |
| June           | 3.93                 |
| July           | 1.53                 |

3.2. Correlation among the weather, water temperature data, and the organic content of sea sludge
Environmental data such as water temperature and weather conditions were collected from relevant public institutions (e.g. the Japan Weather Association), in order to see their influence on the dynamic fluctuations of organic content of the sea sludge. Although sample collections were mainly done on days with fair weather condition, the weather of previous days might affect the composition of the sludge. Meanwhile, changes in water temperature might also influence the composition of the sludge.

Interestingly, we found that the temperature and the preceding weather of September 2016 (9/27) and June 2017 (6/28), as well as the mean water temperature of the relevant week, were drastically increased. Another fluctuation in mean water temperature of the week and/or preceding weather was also observed surrounding the December 2016 (12/22) sampling, with seawater temperature at 20 ºC, and the weather was cloudy with temporary rain, but sunny or cloudy then sunny for the preceding three days (table 4).

Meanwhile, a sunny weather condition was observed on the sampling dates where the organic contents of samples were categorized as "usual". This result indicates a possible effect of external environment to the compositional fluctuations of the sea sludge. The results of organic content changes...
over time were plotted on figure 2, together with seawater temperature changes. Weather conditions are shown on table 4.

![Figure 2. Change of organic contents with water temperature.](image)

4. Discussion
The composition of sea sludge, including the organic matter composition, varies from one locality to another. Such composition is affected by many external factors, including, but not limited to, living organisms inhabiting the area, water temperature, salinity, local climate, terrestrial debris flowing in from the river [1]. This has caused difficulties in defining the sea sludge based on a standardized chemical composition [6]. Meanwhile, research on local variations of sea sludge in an area has been meager. To our knowledge, there has been no study on the chemical compositional changes over time of sea sludge collected from a single locality. The lack of such information hampers an objective discussion about standardized compositional changes of sea sludge.

In this study, we followed the organic content of sea sludge collected from one sampling locality, and discussed our result together with the seawater temperature fluctuations and changes in weather conditions.

4.1. The possible role of microbial activities
A data plot of weekly seawater temperature and sea sludge organic matter composition over time (figure 2) shows that the two changes are congruent, indicating possible correlations. For example, during the months of July 2016 to November 2016, organic content and temperature showed similar fluctuation patterns, with the organic content lagged behind for one month. Water temperature peaked in August then decreased, while the organic content's peak was in September, and then decreased.

Such changes in organic content, when discussed with changes in water temperature, can be explained by considering the presence of microbes. Water temperature increased above 25 °C during the summer months (June to August), and decreases afterwards. Such warm temperature is conducive for microbial activities. We thus suggest that microbial activities might be strongly related to the increase of organic matter in the seafloor sludge. The one-month lag of the organic content peak could also be explained with the microbial activities. The organic matters produced by the microbes accumulate in a process that peaked a month after the actual peak of microbe activities. When the season gradually enters autumn, water temperature drops, and microbe activities slowed down, causing the production of organic matters and its inclusion in the sea sludge, to also gradually drop down.
Table 4. Weather conditions on and up to three days before the collection day.

| Year | Date  | Conditions                   | Year | Date  | Conditions                   |
|------|-------|------------------------------|------|-------|------------------------------|
| 2016 | 7/17  | Cloudy then sunny            | 2017 | 1/22  | Cloudy the sunny             |
|      | 7/18  | Cloudy then sunny            |      |       | Sunny then rain              |
|      | 7/19  | Sunny                        |      | 1/23  | Sunny then rain              |
|      | 7/20* | Sunny                        |      | 1/24  | Snow later rain              |
|      | 8/16  | Cloudy then sunny            |      | 1/25* | Sunny                        |
|      | 8/17  | Cloudy then sunny            |      | 2/23  | Rain then cloudy             |
|      | 8/18  | Cloudy then sunny            |      | 2/24  | Cloudy and sometimes sunny   |
|      | 8/19* | Cloudy then sunny            |      | 2/25  | Sunny                        |
|      | 9/24  | Cloudy then rain             |      | 2/26* | Cloudy                        |
|      | 9/25  | Cloudy then rain             |      |       | Sunny the rain               |
|      | 9/26  | Rain then cloudy             |      | 3/26  | Sunny the rain               |
|      | 9/27* | Mostly sunny and cloudy      |      | 3/27  | Cloudy then sunny             |
|      | 10/28 | Cloudy then rain             |      | 3/28  | Cloudy then sunny             |
|      | 10/29 | Cloudy then sunny            |      | 3/29* | Cloudy and sometimes sunny   |
|      | 10/30 | Sunny                        |      | 4/22  | Cloudy then sunny             |
|      | 10/31*| Cloudy                       |      | 4/23  | Sunny                        |
|      | 11/26 | Sunny then rain              |      | 4/23* | Mostly sunny and cloudy      |
|      | 11/27 | Rain then cloudy             |      |       | Mostly sunny and cloudy      |
|      | 11/28 | Cloudy then sunny            |      | 5/22  | Sunny                        |
|      | 11/29*| Sunny                       |      | 5/23  | Mostly sunny and cloudy      |
|      | 12/19 | Cloudy then sunny            |      | 5/24* | Rain                         |
|      | 12/20 | Cloudy then sunny            |      |       | Rain then cloudy             |
|      | 12/21 | Cloudy with temporary rain   |      | 6/26  | Cloudy then rain             |
|      | 12/22 | Cloudy with temporary rain   |      | 6/27  | Cloudy then rain             |
|      |       |                              |      | 6/28* | Rain then cloudy             |
|      |       |                              |      | 7/22  | Cloudy                        |
|      |       |                              |      | 7/23  | Cloudy                        |
|      |       |                              |      | 7/24  | Cloudy and sometimes sunny   |
|      |       |                              |      | 7/25* | Cloudy                        |

*) Collection day

Figure 3. Collecting sites: (A) for samples from February 2017, (B) for samples from July 2017. Notice algal growth and disappearance on the collection sites.
4.2. The possible influence of algal life cycle

While a peak and gradual decrease in organic content were explicable with an increase in microbial activities caused by high water temperature, a deep drop in organic content, such as what was observed in February 2017, could not be explained similarly. Water temperature drops down gradually, and starting from November 2016 and all the way to June 2017, the temperatures stayed below 25 °C despite small fluctuations. Since such low seawater temperatures could not support microbial activities, other environmental factors must be considered to explain the steep drop in the organic content of sea sludge. Interestingly, we also observed the emergence of algal-bed (figure 3) at the sample-collecting locality in January 2017.

Taking everything into account, we therefore suggest that drastic fluctuations in organic content for the non-summer months could be explained in two steps. First, conducive water-temperature during summer triggered microbial activities, causing organic content to be released into the sea sludge. When water temperature dropped down after summer, the organic content of the sea sludge was still high, and it was then used as nutrients by the alga to grow into an algal-bed (figure 3(A)). Because microbial activity significantly decreased during the non-summer months, the organic content was not replenished, causing a gradual decrease in organic matter presence during the months of November 2016 to April 2017.

We observed in situ that the algal-bed disappeared by March 2017 (figure 3(B)), while the organic content gradually increased during the months of February and April 2017, although it did not peak. We hypothesized that the life cycle of the alga could explain this observation. The alga might reach the end of the life cycle, which could partially be caused by the decrease of organic matter nutrients contained in the sea bottom sludge. Despite the non-optimal temperature in February to April, a slow decomposition process by microbes might still happen. Dead alga then decomposed, causing a gradual increase of organic matter during the months of March and April 2017.

4.3. The correlation between weather conditions and changes in organic content

Other non-biological factor might also affect the changes of organic content of the sea floor sludge collected from Hidaka Port in Wakayama. We observed that between April and July 2017, the organic content decreased to 0.47% in May 2017, and increased to 2.51% in June 2017. This sudden and drastic change could also be explained by non-biological causes, such as local weather on the week of sampling date. Our previous study has shown that heavy rains could cause nutrients, salts, and organic matter contained in coastal sea sludge to decrease, probably due to washing-away caused by the sudden increase of freshwater [2]. However, we also did not rule out the possibility of a sudden increase of organic content caused by heavy rains happened inland. Such rain could cause organic materials from terrestrial agents brought down by the river to the sea, and deposited on the coastal sea floor sludge.

Data on the three-days leading to and on the sample-collecting day showed that there was a heavy rain for four days, around the sampling date of May 2017 (table 4). This might have caused the decrease of organic content. Meanwhile, several days before the sampling day of June 2016, heavy rain also happened inland. This might have caused terrestrial organic matters to be brought in to the sea (figure 4). Then, several days of calm weather might have let the terrestrial organic components to settle at the bottom, causing a sudden increase in organic content of the sea sludge.
5. Conclusion and Future Directions
Our result reported here indicates possible explanations for the changes of organic content in natural sea sludge:

1. Change of organic content matches the change of seawater temperature with one-month lag, especially during summer. High water temperature during summer might have caused increased microbial activities.
2. The decrease of organic content during the months of autumn and winter could be caused by the algal lifecycle, which might include feeding on organic materials in the sludge.
3. Weather changes might affect the organic content in the sea sludge, since heavy rains might leach the organic matters inside the sludge. The heavy rains occurred inland might have brought organic matter into the coastal waters, and its deposition might cause an increase in the sea floor sludge organic content.

The elucidation of organic contents also might allow for future studies aiming at the detection of changes in other chemical components such as inorganic matter. Future studies on (1) detailed analyses of chemical compositional changes for the course of multiple years, (2) similar studies on several other localities will be needed to not only reconfirm our result presented here, but also to gain a more detailed picture of the interaction between sea sludge chemical composition dynamics and the external environment. Moreover, studies on microbial activities are also crucial, in order to decisively elucidate the actual mechanisms of the changes. For example, in this study only three possible causes of the dynamics of the sea sludge organic content were discussed. However, there are other possible reasons to explore, such as farming activities. Accordingly, future studies in a more comprehensive manner spanning multiple years, involving samples of different sites and multiple loci are warranted.

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References
[1] Yoshida T A 1974 About generation and the removal of the sludge - In bottom sampler examination of the Gulf of Minamata J. Hedoro 11-27 (In Japanese)
[2] Hirano H, Sasahara R, Morita Y, Okamoto K, and Hotta K 2011 Purification of Sludge by Micro-Bubble and Microorganisms Activator-Case of Using Enzyme, Collection of papers: Annual Conference in CST 723-724 (In Japanese)

[3] Nakao A 2012 Cesium adsorption and fixation on soils trend in the science 17(10) 10_40-10_45

[4] Hirano H, Toyama T, Nishimiya N, and Okamoto K 2015 Removal of cesium from sea sludge through decomposition of organic matter with aqueous hydrogen peroxide International Journal of GEOMATE 8(1) 1203-1206 (In Japanese)

[5] Hirano H, Uragaki Y, and Morita S 2016 Preparation of prototype artificial sludge based on compositional information of sea sludge Part 2: Improvement idea about content 50th Annual Conference of Japan Society on Water Environment p.190

[6] Hirano H, Toyama T, Nishimiya N, Setiamarga DHE, Morita S, Uragaki Y, and Okamoto K 2017 Artificial sludge based on compositional information of a natural sea sludge International Journal of GEOMATE 12(31) 95-99