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学位論文全文に代わる要約
Extended Summary in Lieu of Dissertation

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学位論文題目：
Title of Dissertation

Studies on biophilic elements and nutrient regeneration in the coastal sediments
（沿岸海域における堆積物中の生元素と栄養塩溶出に関する研究）

学位論文要約：
Dissertation Summary

Coastal environments are easily effected by human activity, particularly where the aquaculture is actively conducted. The major anthropogenic sources of organic matter and nutrients around the coastal areas, included wastewater from urban and industrial areas, and also organic-rich wastes from aquaculture which can have significant impact on the coastal sediments. To understand the biochemical processes of the coastal sediments, the comprehensive data set of chemical, physical, geological, and biological processes, which control the composition of the materials in this environment, were required.

The study site of this research is a small enclosed bay, Shido Bay, where is a typical coastal sea. This bay is surrounded by populated areas with about 10,000 people living around the bay and also this bay is an active aquaculture field. Shido Bay is made up by two coastal areas, Tamaura Bay and Nagahama Estuary, and receive fresh water input from Kabe River. The important economic activity of Shido Bay is marine aquaculture such as fish and oyster, which are located entire the Bay. Large amount of organic wasted matter (uneaten fish feed and faces) were continuously generated from aquaculture, and also wastewater from urban areas were discharged into this area. Organic matter and heavy metals in seawater may increase their concentrations and it probably become a problem of organic and heavy metal pollutions in coastal environment. Furthermore, high organic matter and heavy metal loading from natural and anthropogenic system were accumulated and distributed on the surface sediments. The large amount of organic matter can be remained in the bottom sediments, and it can be released from coastal sediment to overlying water by nutrient regeneration as available nutrients for primary producer again. This Ph.D. thesis was a research of the biogeochemical processes of biophilic elements and the controlling factor on nutrient regeneration in a semi-enclosed coastal environment. The major objectives of the present research are as follows:

1) To determine the horizontal distribution of major physicochemical parameters (i.e. water content,

sediment grain-size, total organic carbon (TOC), total nitrogen (TN), total phosphorus (TP) and AVS content) of the coastal surface sediments, discuss the source of those materials in the sediments and study their interaction to provide an information on environmental pollutions resulting from aquaculture activity.

2) To investigate the content and distributions of heavy metals (Cd, Cu, Pb, Zn, Mn, As, Cr, Ni and Co) in the surface sediment in order to evaluate the heavy metals contaminations and pollutions.

3) To study the behavior of the phosphorus in the surface sediment and discuss the impact of the organic waste to the surrounding areas of the fish farms, using the phosphorus as an indicator.

4) To evaluate nutrient (DIN, $Si(OH)_4$ and PO_4) regenerations from the sediment core incubation experiment and examine the effect of benthic organisms on measuring nutrient upward fluxes.

5) To determine the influence of superficial sediment layer (a 2-3 mm of the top of surface sediments) on the nutrient upward fluxes at the sediment-water interface and to explain the characteristic of superficial layer.

6) To study the effect of bacterial activity on measuring nutrient upward fluxes and evaluate controlling factor on nutrient regeneration.

The study on biophilic elements and nutrient regeneration in the coastal sediments involved multidisciplinary scientific study of chemical, physical, geological, and biological processes which control the composition of the materials in natural environment. In this study, at first, the horizontal distribution of organic matter and heavy metal content in surface sediments were determined, and second, nutrient regenerations at sediment-water interface were measured. The overview of the present study was showed in Fig. 5.

Surface sediments in coastal environment

Shido Bay is a small enclosed bay, where is surrounded by populated areas with about 10,000 people living around the bay and an aquaculture is conducted actively. This area has very complex hydrodynamics, resulting in a wide variety of sedimentary environments despite the relatively small area. Aquaculture production in Shido Bay reached a high in 1990 of 2841 tons of fish, 149 tons of oyster and 234 tons of nori production, but the production decreased in 2001 by 28, 6, and 41% for fish, oyster, and nori production, respectively. The number of fish cages and oyster farms decreased due to the economic recession. The quality of surface sediments of small embayment as Shido Bay is influenced by the primary production, organic matter loading from river and aquaculture field. In this study, we determined the horizontal distribution of organic matter and heavy metal content in surface sediments in order to clearly understand the sediment condition and

to ensure the sustainability of aquaculture.

Surface sediments were collected at 63 stations in May–July, 2011 in Harima Nada and 29 stations in June–July, 2012 in Shido Bay (the Seto Inland Sea, Japan) as showed in Fig. 1. The horizontal distributions of total organic carbon (TOC), total nitrogen (TN), and total phosphorus (TP) in the surface sediments of two coastal areas, almost non-fish farm area, Harima Nada and an intensive fish farm area, Shido Bay, were determined to investigated the impact of the organic waste from the fish farm to the surrounding areas, using the phosphorus as an indicator.

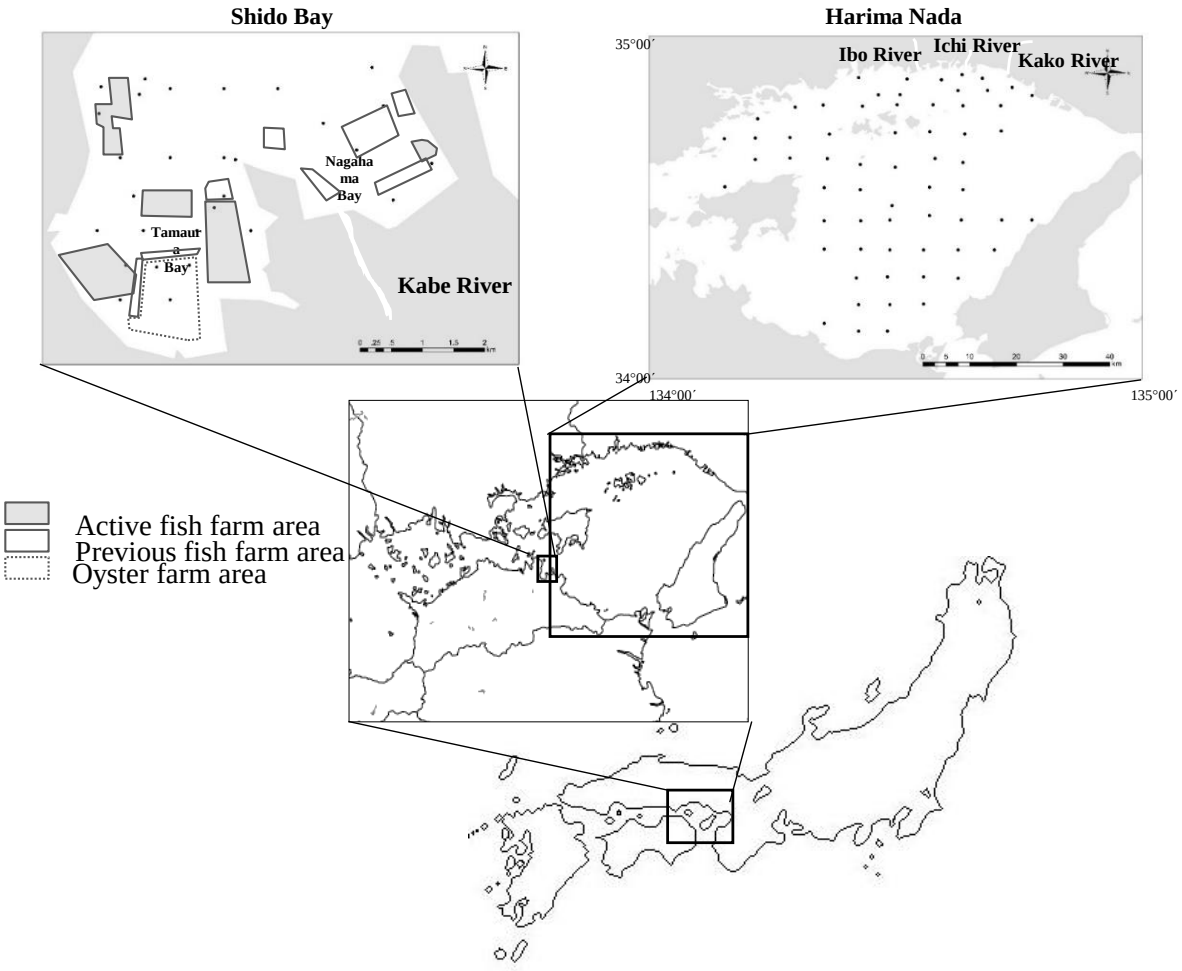

Fig. 1 Study sites and sampling stations in Harima Nada and Shido Bay, the Seto Inland Sea and status of aquaculture such as fish farms and oyster farms in Shido Bay

TOC, TN and TP distributions in surface sediments were similar in two areas (Fig. 2), except for partly higher TP content in fish farm areas (Fig. 2(c)). In Shido Bay, there was a good correlation between TOC and TN ($r^2 = 0.985$), but no correlations between TP with TOC and TN, respectively, although a good correlation of

TOC, TN and TP were observed in Harima Nada. These different correlations between TP and TOC or TN in two areas suggested different phosphorus source in the two areas. It was thought that the partly high phosphorous content in Shido Bay was originated from the residue of fish farm activities, whereas the TP in the surface sediments of Harima Nada was come from settling organic matter originated from phytoplankton. This study suggested that higher TP content predicted from TOC and TN content was characteristic of fish farm area, and TP content was a good indicator of effect of fish farming.

Moreover, total organic carbon (TOC), total nitrogen (TN), total phosphorus (TP), water content, grain size and heavy metals (Cd, Cu, Pb, Zn, Mn, As, Cr, Ni, Co, Al, Fe and Li) in surface sediment were determined at 29 sites in Shido Bay. The sediment in this study area had higher mud content (7.03–72.59%, mean 40.46±15.81%) in the inner part of Shido Bay than in the mouth. The horizontal distributions of TOC, TN and heavy metals (except Co and Mn) of Shido Bay and Harima Nada were quite similar and were significantly related to the mud content. On the other hand, high TP and Ca-bound phosphorus content were observed at the eastern and western part of Shido Bay where fish cage were located nearby, because of the residue of fish feed which was refractory compounds, and lower TP content was found in the middle part where oyster farms were operated.

It was thought that the aquaculture activities in Shido Bay affected the amount of organic matter in this area, because a higher organic matter content were observed near fish cages, and the increase of organic matter content from 2001 to 2012 in aquaculture area was observed. Moreover, the atomic C/N ratios in Shido Bay (6.3 to 10.5) were lower than that of terrestrial matter (e.g. 20–85). Nevertheless, the study area in the present work was not contaminated by heavy metals, judging from the comparison with sediment quality guidelines and the heavy metal content found in other marine environments in the Seto Inland Sea. Also, the relative enrichment factor (EF value) used for evaluating heavy metal contamination had a value close to 1, which showed that the heavy metals in the surface sediment of this area was a background level of sediment and did not come from aquaculture activity or other sources. This study indicated that primary production was a main source of organic matter found in the sediment of Shido Bay, fish and oyster farming was also influenced on the organic matter accumulation on surface sediment, but aquaculture activity did not influence heavy metal contamination in the surface sediments, although the horizontal distribution of organic matter and heavy metals (except Co and Mn) were quite similar and were significantly related to mud content.

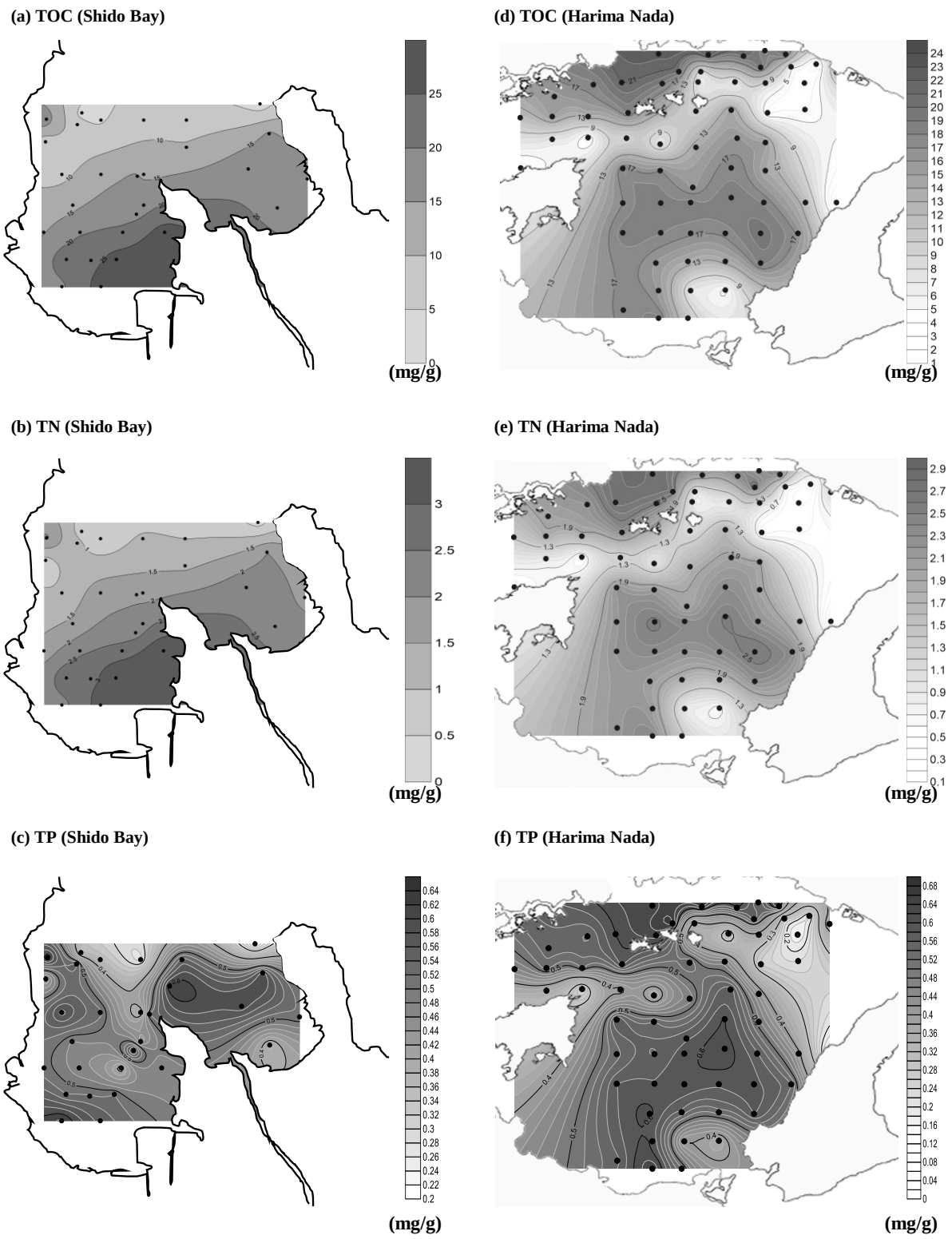

Fig. 2 Horizontal distribution of TOC, TN, and TP in the surface sediment of Shido Bay (a, b, c) and Harima Nada (d, e, f).

Nutrient regeneration at sediment-water interface in coastal environment

Surface sediment acts not only as a sink of organic matter deposition, but also a source of nutrients (N, P and Si) release from the sediment to overlying water particularly in shallow coastal system. When the organic matter is accumulated on surface sediments, the decomposition of the organic matters regenerate N, P and Si as their soluble forms of nutrients. In this study, nutrient upward fluxes were estimated by core incubation method, which is the most popular method. We conducted monthly observations from April 2015 to January 2016 to measure nutrient fluxes and examine the effect of benthic fauna on measuring nutrient upward fluxes in the middle part of Shido Bay. The biomass of benthic communities in this area increased in warm season. The composition of the benthic communities, according to taxonomic group, was dominated by Polychaeta composed of a few species of Capitellida and Spionidae. Nutrient fluxes of DIN (NO_3+NO_2+NH_4), PO_4 and $Si(OH)_4$ increased with the increase of temperature. Nevertheless, the relationship between nutrient fluxes and density of organisms in the benthic communities was not observed. We concluded that the nutrient fluxes were not regulated by benthic fauna in the core sediment, but by temperature.

Moreover, the superficial sediment layer (SL), which is the top 2-3 mm of the surface sediment, is directly received high particulate organic loading. Accordingly, the superficial sediment layer may contribute high nutrients regeneration at the sediment-water interface. Therefore, this study will describe characteristics and role of the superficial layer on surface sediments. The seasonal variation of TOC, TN, Chl *a* (Chlorophyll *a*) and Pheo. (Pheo-pigments) of superficial layer and subsurface layer (0–1 cm and 1–2 cm) were measured. TOC and TN were relatively constant in three layers during study period. In contrast, total pigments (Chl *a* and Pheo.) were often higher in superficial layer than subsurface sediments.

Nutrient fluxes (NH_4, PO_4 and $Si(OH)_4$) were also measured from the core incubation experiments of six undisturbed sediment cores under *in situ* temperature (Fig. 3). Core incubations were conducted for triplicate total fluxes and triplicate SL-less fluxes. Nutrient fluxes (NH_4, PO_4 and $Si(OH)_4$) of the core incubation experiments in early summer (May to August 2014) were higher than in winter (December 2013 to February 2014), and the nutrient fluxes were regulated by the temperature of each season (Fig. 4). Furthermore, the results of some experiments showed that total fluxes were higher than SL-less fluxes. Moreover, in the low temperature season, the SL seemed to absorb nutrients, probably due to the microphytobenthos photosynthesis which assimilated nutrients under the sufficient light penetration to the seafloor, because the transparency increased in winter. These results suggested that SL played an important role on nutrient regeneration, and it acted as source and sink of nutrients in shallow water. The SL was an

active layer, which had an impact on nutrient upward flux in some cases and also took up nutrient upward in surface sediment in some cases. Moreover, the difference in quality of contained substance in superficial layer may reflect nutrient regeneration such as organic tissue, diatom frustule or bacteria. However, negligible effect of the benthic fauna on measuring the nutrient upward fluxes from coastal sediments was found in this area.

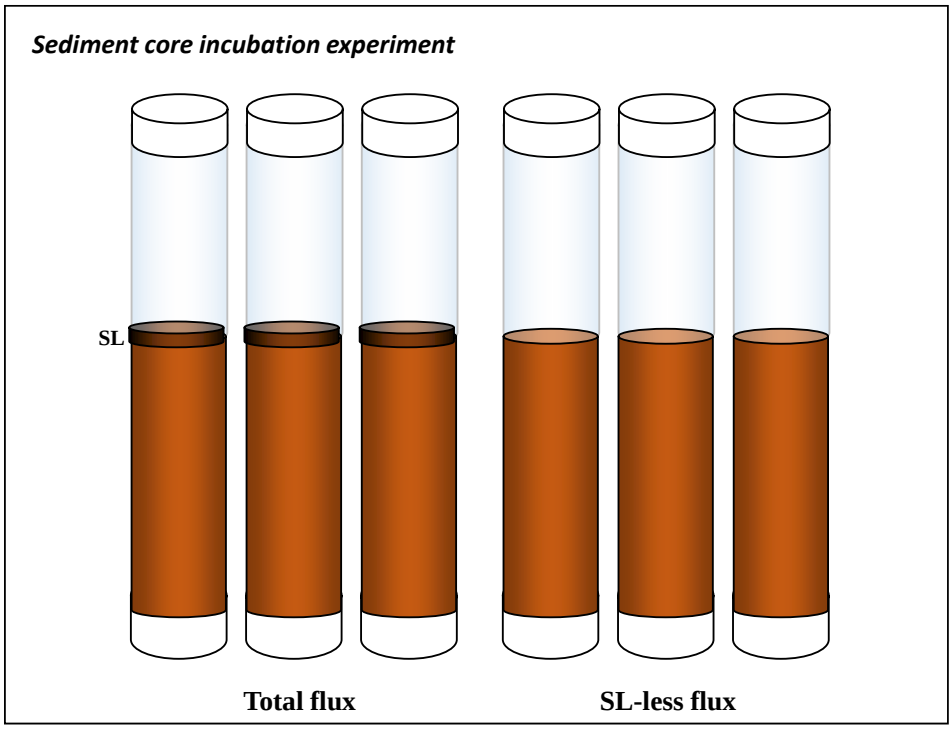

Fig. 3 Laboratory core incubation experiments for upward nutrient flux of Total flux and SL-less

The effect of bacterial and microphytobenthos nutrient uptake on the nutrient budget in the overlying water should be an important factor to consider the nutrient fluxes. Furthermore, the clear effect of bacteria and microphytobenthos activities on upward nutrient fluxes were observed in high temperature season, May to September 2016. In core incubation experiments, sodium azide (NaN_3) was added to the overlying water of core incubation system to inhibit bacterial activity. When NaN_3 was not added in sediment cores, nutrient fluxes from sediment to water column were higher than the fluxes of NH_4, $Si(OH)_4$ and PO_4 in NaN_3 adding experiments. In NaN_3 adding experiment, nutrient fluxes would be regulated by only the physico-chemical processes. This results indicated that upward nutrient fluxes can be affected by bacteria activity, because the activities of microphytobenthos was only high during winter. As described in chapter 4, microphytobenthos was active only during winter period when sufficient light penetrated to the seafloor.

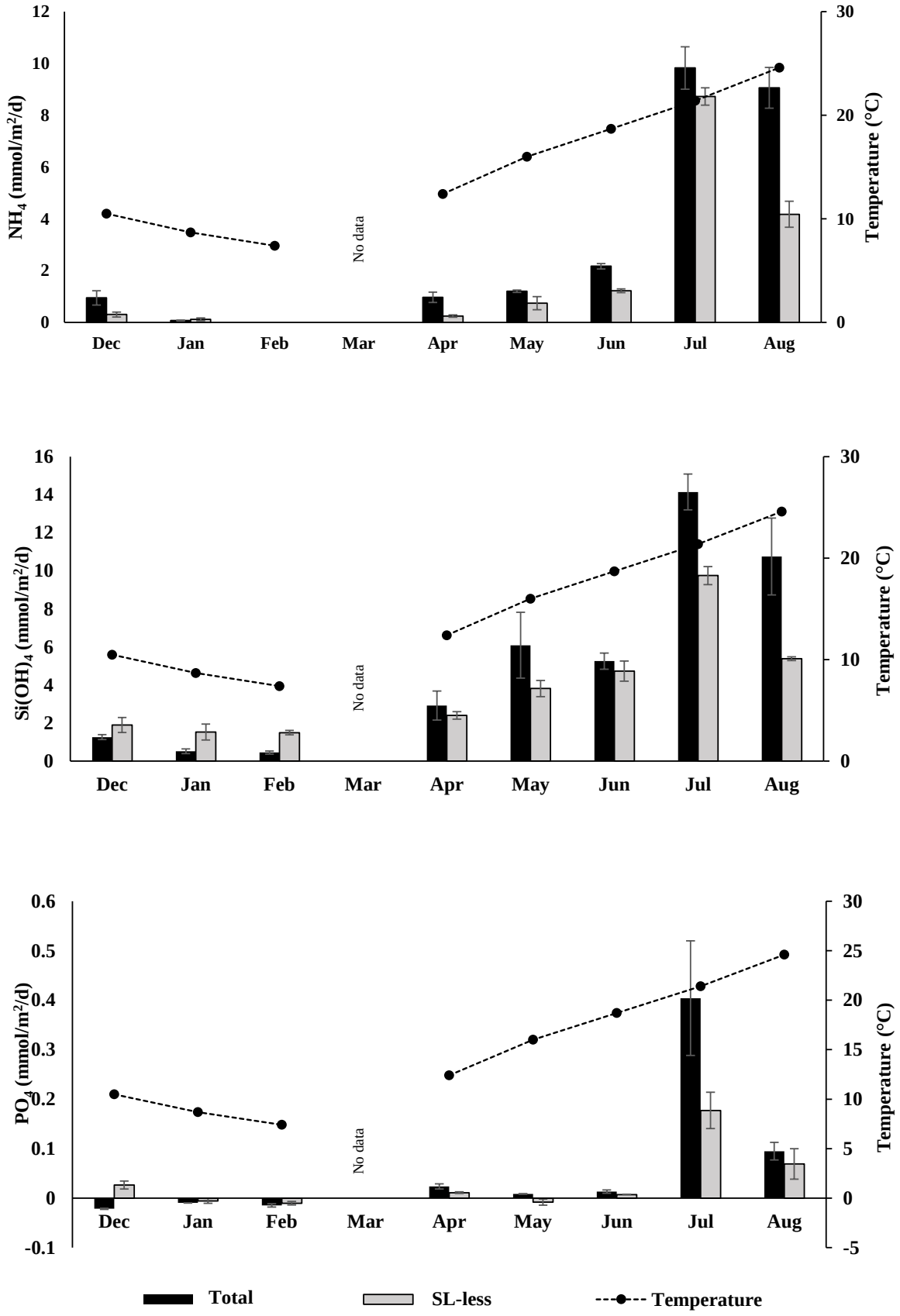

Fig. 4 Nutrient flux of NH_4, $Si(OH)_4$, and PO_4 (mmol/m^2/d) and surface sediment temperature (°C)

*SL-less means the sediment core which SL layer is removed

Factor controlling organic matter and nutrient regeneration in coastal sediments

This study showed the overall of factor controlling biophilic elements and nutrient regeneration in shallow coastal system (Fig. 5). Organic matter on surface sediments of small embayment is influenced by the organic matter loading from primary production in the water column and from the land. Also, it is influenced by the aquaculture activity, where aquaculture field is located. In Shido Bay, organic matter loading from the land and river was not noticeable, because an atomic C/N ratio on surface sediments (6.3–10.5) was similar to the C/N ratio in Redfield ratio (6.6). The results indicated that the primary source of organic matter was the primary production by phytoplankton in water column. Moreover, aquaculture activity also another factor generated high content of organic matter and accumulated to the bottom sediment near the fish cages.

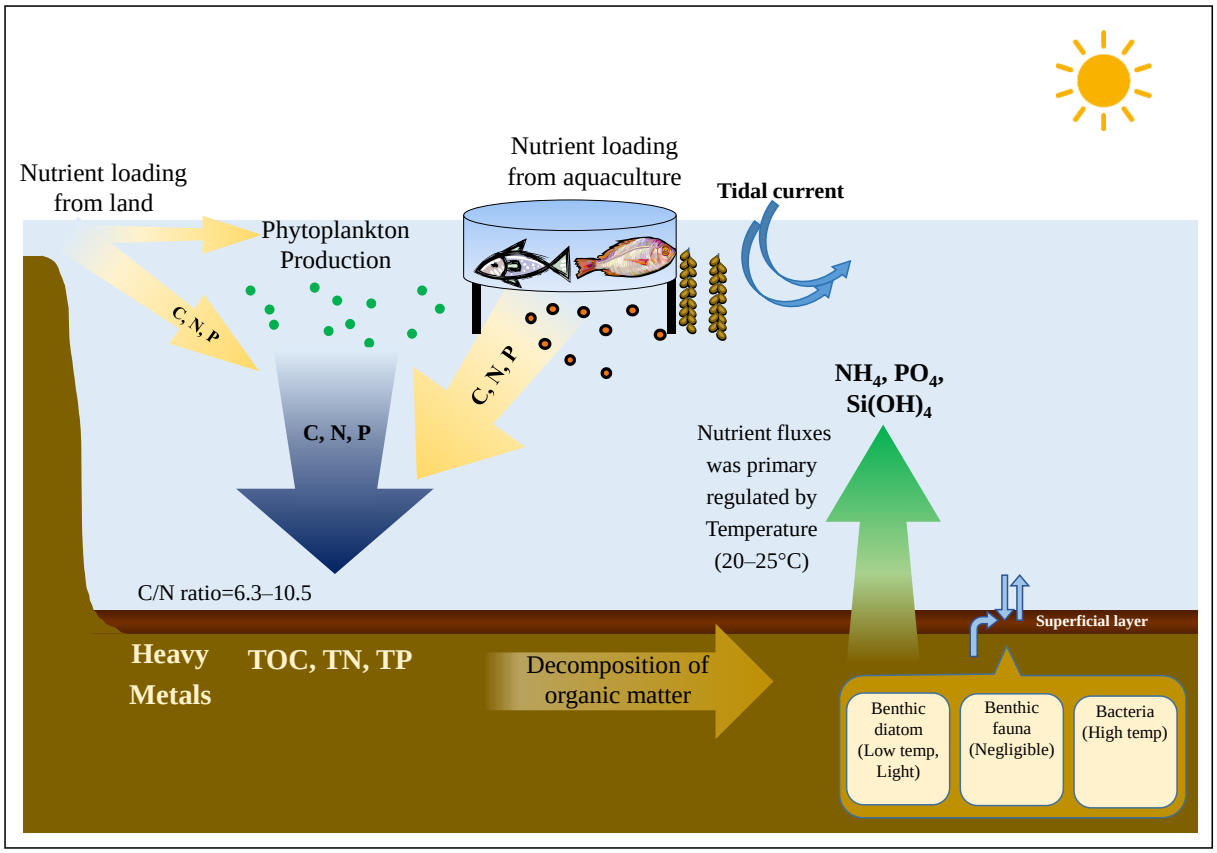

Fig. 5 Schematic of source of biophelic elements and nutrient regeneration in shallow coastal environments

It was thought that surface sediment played as a sink of organic matter deposition, and also it is a source of nutrients regeneration from the sediment to overlying water particularly in shallow coastal system. In coastal environment, upward nutrient flux was fundamentally regulated by temperature, and high temperature period

promoted high nutrient fluxes. In addition, it was thought that biological factors as benthic fauna, microphytobenthos and bacteria metabolisms were influenced to nutrient regeneration processes. Bacterial and microphytobenthos activities were important on nutrient regeneration on shallow coastal system, because the effect of benthic fauna on nutrient regeneration was negligible. Moreover, bacterial activity was a major biological factor, because microphytobenthos (benthic diatom) was active only during winter period when sufficient light penetrated to the sea bottom.