Remediation of coastal marine sediments using granulated coal ash

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Abstract

It is very important to reduce phosphorus flux from sediment as well as cutting down terrigenous loads in order to control eutrophication in semi-enclosed coastal seas. Hydrogen sulfide is also a noxious substance which is highly toxic and fatal to benthic organisms. The purpose of this study is to evaluate remediation efficiency of organically enriched sediments using granulated coal ash (GCA) in terms of reducing benthic phosphorus flux and hydrogen sulfide. A flow-through experimental system was used to simulate the semi-enclosed water bodies. The application of GCA decreased the concentration of PO_4^{3-} in the pore water effectively, and reduced phosphate releasing flux from the sediment into overlying water by 37-44% compared to the control. The hydrogen sulfide in the pore water was also decreased by 77-100%, due to adsorption onto the GCA and deactivation of sulfate-reducing bacteria due to increasing pH. Thus, GCA is a promising recycled material for reducing phosphate releasing flux from organically-enriched sediment to alleviate eutrophication as well as reduce the concentration of hydrogen sulfide in pore water.

Key words

enclosed water body, hydrogen sulfide, coal ash, marine sediment, thermal power station, phosphate

1. Introduction

The Seto Inland Sea is the largest enclosed sea located in the western part of Japan. In such enclosed water bodies, massive growth of algae has been observed every year often leading to high consumption of dissolved oxygen owing to decomposition of dead cells [1, 2]. Oxygen depletion is fatal to organisms and brings much economic losses to aquaculture industries. One of the reasons why the massive growth of algae occurs is the significant phosphate supply from organically enriched sediments accumulated on the bottom of enclosed water bodies located in areas off the coast of large cities.

For example, the phosphate releasing flux from the sediment into seawater is twice higher than that of terrigenous loads to Hiroshima Bay, which is located on the western part of the Seto Inland Sea and dotted with many small inlets [3]. Therefore, it is an important strategy to reduce phosphorus flux from the sediment as well as cutting down terrigenous loads to alleviate eutrophication.

Furthermore, hydrogen sulfide (H_2S) is produced in the sediments through reduction of sulfate ions by sulfate-reducing bacteria [4]. Hydrogen sulfide is harmful for living organisms, and consumes oxygen when it is oxidized. In Japan, 0.2 mg/g of acid volatile sulfide (AVS; not only H_2S but also including several sulfur compounds) is proposed as a cut-off criterion for sustainable aquaculture in coastal seas [5]. However, in reality, the sediments in approximately half of the Seto Inland Sea where is one of the major centers for aquaculture activity in Japan do not meet the AVS criterion [6]. Thus, it is important to reduce hydrogen sulfide concentration in the sediments to restore and maintain healthy aquatic ecosystems.

Granulated coal ash (GCA) is a by-product from coal thermal power stations. In 2005, 11 Mt of coal ash was generated from coal thermal power stations and other industries in Japan [7]. Coal ash is classified into two categories: bottom ash generated in boilers and fly ash from waste gas treatment process, the latter comprising 85-95% of total coal ash. The GCA used in this study is the product of mixing granulated fly ash with cement as a binder. Generally, GCA has been used only for road beds, construction material and coarse aggregates for concrete. Therefore, new applications utilizing by-product from coal thermal power stations are expected to contribute towards promoting recycling consciousness and waste reduction within the society.

Previous studies have proven that GCA adsorbed hydrogen sulfide and phosphate in seawater efficiently in batch experiments [8, 9]. GCA can reduce concentration of phosphate effectively even though the sediment conditions are highly reductive in which iron type amendments cannot be applied [8]. Furthermore GCA has a high adsorption capacity for hydrogen sulfide compared to other materials [9]. Thus, GCA is more suitable than any other material for remediation of enclosed water bodies where the sediment condition are generally very reductive with observed significant phosphate releasing flux and hydrogen sulfide generation. However, there have not been much scientific reports on the application of GCA for remediation of organically enriched sediments compared with other materials such as steel-making slag [10-12]. As far as we know, this study will provide the initial observations needed in developing an amendment for organically-enriched sediment remediation using containers to simulate enclosed water bodies and to prove the phosphate and hydrogen sulfide removal efficiency of GCA. This proposed simple remediation technology involving the addition of GCA to organically-enriched sediments is also promising for coastal environmental remediation efforts in many developing countries where expensive remediation technology is generally unavailable and impractical.

The purpose of the present study is to evaluate remediation efficiency of GCA application to organically enriched sediments in terms of reducing hydrogen sulfide and phosphate using container experiments with flow through system simulating enclosed water bodies.

2. Materials and methods

2.1. Granulated coal ash (GCA)

The GCA used in this study is a commercially-sold product, named 'Hi-beads' (Energia Eco Materia Co., Inc.) with 5 mm diameter, which is produced through the granulation process of pulverized fly ash from coal firing systems generated from thermal power stations (Chugoku Electric Power Co. Inc.) with added cement as binder amounting to 15% of the final product.

Previous studies showed the GCA is mainly composed of SiO_2, CO_3, Al_2O_3 , CaO, C and Fe_2O_3 with quartz and aluminosilicate crystal phase, and their concentrations are 395, 133, 126, 55.4, 27.4 and 22.5 g/kg, respectively [13]. The environmentally regulated substances dissolved from the GCA used in this study were obviously below the standard levels for environmental criteria in Japan [13].

2.2. Container experiments

2.2.1 Experimental settings

The container experiment was designed to simulate an enclosed water body (Fig. 1). The experiment was conducted from August 27th to October 10th in 2007. The GCA and sediments (described below) were mixed in round black polyethylene containers (ϕ: 550 mm, h: 420 mm), and sand-filtered natural seawater was supplied and allowed to overflow at an exchange rate of 0.7/d, which is the average exchange rate of seawater between the upper and lower layers of the water column in the northern part of Hiroshima Bay. These containers were placed in a water bath (1000 L FRP container) to prevent rapid water temperature changes during the experimental period. The light intensity was adjusted to 50-120 μmol/m^2/s to simulate the conditions of shallow coastal areas using loosely-woven nylon black sheets (cheese cloth) placed over the containers.

The sediment was collected from the Ohzu Inlet located at the head of Hiroshima Bay where it is affected by high terrigenous nutrient load from Hiroshima city and where seawater exchange is very low. Debris and pebbles were removed from the sediments before use. In the experimental container, 50 L of sediment and 50 L of the GCA were mixed, while 50 L of sediment without the GCA was used as a control. The container experiment was conducted in triplicates.

The black colored organically enriched sediment collected here shows highly reduced condition with pungent smell caused by ammonia and hydrogen sulfide. This situation may be similar to conditions observed in coastal areas adjacent to large cities in Japan and many developing countries.

2.2.2 Overlying seawater analyses

Overlying seawater samples were collected at Day 0 (initial), 9, 25, 35 and 45 after mixing GCA with the sediment. Water temperature, salinity and pH were measured directly by dropping a multiple electrode (U-10, Horiba) into the container on site. The overlying water samples for dissolved oxygen (DO) and nutrients analyses were collected 5 cm apart from the top of the sediment by a siphon tube. DO was determined by Winkler method on site [14]. The overlying water samples for nutrients analyses were filtered through 0.45 μm membrane filters (MILLEX-HV, Millipore) and transported to a laboratory under cool and dark conditions inside an ice chest.Thereafter, the concentrations of PO_4-P, NH_4-N, NO_2-N and NO_3-N were determined by standard methods [14] (ascorbic acid reduction molybdate blue adsorption spectrophotometry, indophenol blue method, N-(1-naphthyl)-ethylenediamine adsorption spectrophotometry and Cd-Cu reduction N- (1-naphthyl)- ethylenediamine adsorption spectrophotometry, respectively) using an auto analyzer (SWATT, BLTEC).

2.2.3 Sediment analyses

Sediment samples for sediment quality analysis and pore water analysis were collected at Day 0 (initial and just after the mixing with the GCA), 9, 25, 35 and 45 after mixing GCA with the sediment. Sediment cores were sampled using a cylindrical Tupperware canister (ϕ: 77 mm, h: 47 mm), and pH and oxidation and reduction potential (ORP) were measured immediately using electrodes (PRN-40, Fujiwara, RM-12P, TOA DK). Thereafter, the Tupperware canisters were sealed and transported to the laboratory under cool and dark conditions inside an ice chest.

2.2.4 Pore water analyses

The sediment samples were centrifuged at 3,500 rpm for 10 min to separate pore water from the sediment. Unfiltered sample was used for determining concentration of hydrogen sulfide using a detection tube (200SB, Komyo Rikagaku Kougyo). The rest of the pore water was filtered through a 0.45 μm membrane filter (MILLEX-HV, Millipore) and used for determination of PO_4-P, NH_4-N, NO_2-N, and NO_3-N concentrations. The nutrients were determined by the same methods as the overlying water analyses using an auto analyzer (SWATT, BLTEC).

3. Results

3.1 Overlying water

Throughout the experimental periods, water temperature and salinity of the overlying water did not show statistical significance between the GCA container and control, changing only in the range of 23.6-29.4 °C and 2.85-3.12%, respectively.

The pH of the overlying water of the GCA container was higher than that of the control with a statistical significance ($p<0.01$-0.05) except for Day 25 (Fig. 2).

The DO concentrations in the overlying water of the GCA containers were higher than that of the control after Day 25 (Fig. 3).

The concentration of PO_4^{3-} in the overlying water of the GCA container decreased by 18-31% compared to the control and showed a statistical difference ($p<0.05$) on Day 35 (Fig. 4).

The concentrations of NH_4^+, NO_2^- and NO_3^- in the overlying water are shown in Figs. 5 and 6, respectively. The concentration of NH_4^+ of the overlying water did not show statistical significance between the GCA container and the control. The concentration of NO_2^- and NO_3^- in the overlying water of the GCA container is higher than that of the control with a statistical significance ($p<0.05$) on Day 35.

3.2 Pore water

The concentration of PO_4^{3-} in the pore water of the GCA container decreased by 62-97% compared to the control, and showed a statistical significance ($p<0.01$-0.05) except on Day 45 (Fig. 7).

The concentration of H_2S-S in the pore water of the GCA container decreased by 77-100% compared to the control, and showed a statistical significance ($p<0.05$) on Days 35 and 45 (Fig. 8).

The concentrations of NH_4^+, NO_2^- and NO_3^- in the pore water did not show significant differences between the GCA container and control. However, the concentration of NH_4^+ in the pore water of the control tended to be higher than that of GCA container (Fig. 9), while the concentrations of NO_2^- and NO_3^- in the pore water of the control were higher than that of GCA container except just after the mixing of GCA (Fig. 10).

3.3 Sediment

The pH of the GCA container was higher than that of the control and showed a statistical significance ($p<0.05$) on Days 25 and 45 (Fig. 11).

The ORP of the GCA container was lower than that of the control, and showed a statistical significance ($p<0.01$) on Days 9 and 35 (Fig. 12).

4. Discussion

The pH of the GCA container and the control were 8.2-8.6 and 8.0-8.3 for overlying waters and 6.7-8.9 and 6.7-7.5 for sediments, respectively (Figs. 2, 11). The pH increase in the GCA containers was caused by the hydrolysis of calcium salts such as $CaCO_3$ and $CaCl_2$ [13]. Generally, pH of organically enriched sediment is weakly acidic owing to organic acid generated by the decomposition of organic matter and protons produced by nitrification. The pH range is considered intolerable for sulfate reducing bacteria, because their habitable pH range is 5.5-8.5 [15-17]. Thus,GCA application is effective in the deactivation of such sulfate reducing bacteria as well as for neutralizing sediment pH. On the other hand, the pH increase in the overlying water of the GCA container is within a few values because water exchange rate based on in situ condition (0.7/d) and the carbonate buffer action were considered to have prevented the pH from increasing. Thus, the application of GCA in appropriate amounts will not affect the water column in terms of pH changes.

The DO concentration in the overlying water of the GCA container was higher than that of the control after Day 25 (Fig. 3). The DO concentration of overlying water and NH_4^+ concentrations in pore water indicated almost same pattern until Day 25 between the GCA container and the control (Figs. 3, 9). However, after Day 25, NH_4^+ concentration in pore water of the control was higher than that of GCA container and its evolution corresponded well with the DO decrease seen in the control. Therefore, the DO in the control may been consumed by NH_4^+ oxidation in the pore water, while DO consumption of the GCA container was suppressed compared with the control due to decreasing NH_4^+ in the pore water which consumes oxygen when it is oxidized. Furthermore, the concentration of hydrogen sulfide in the GCA container was also very low compared with the control (Fig. 8), which indicated oxygen consumption required for the oxidation of hydrogen sulfide in the GCA container was suppressed simultaneously compared with the control.

The concentration of PO_4^{3-} in the overlying water of the GCA container was lower than that in the control (Fig. 7). The decrease of PO_4^{3-} concentration of the overlying water in the GCA container is mainly due to the suppression of PO_4^{3-} releasing flux from sediments into overlying water as will be described later.

The concentration of PO_4^{3-} in the pore water in the GCA container also decreased dramatically to 1.2 μM from 38.8 μM after the application of GCA even under highly reductive sediment conditions such as ORP of -328--436 mV (Figs. 7, 12). The significant decrease of PO_4^{3-} concentration is brought by the formation of calcium phosphate on the GCA surface [8]. The GCA contains 55.4 g/kg of calcium oxide and its surface is alkaline [13], which is favorable for the formation of calcium phosphate [18]. Thus, the PO_4^{3-} in the pore water of the GCA container was adsorbed effectively onto the GCA with the precipitation of calcium phosphate.

The phosphate releasing flux from the sediment into the overlying water was calculated as follows: the average phosphate concentration in the seawater supplied to each container was 1.5 μM during the experimental period. The volume of overlying water is 63.4 L and exchanged at a rate of 0.7/d. Thus, the mass of phosphate-P loading into the experimental container is 67 μmol P/d which was calculated by multiplying the phosphate concentration in the overlying water by 63.4 L (volume of the overlying water) and 0.7/d (seawater exchange rate). In this estimate, the adsorbed amount of phosphate was negligible because the adsorption capacity of GCA is poor under low PO_4^{3-} concentration [8]. The phosphate releasing flux from the sediment into overlying water was calculated using the difference of phosphate concentrations between the supplying water and the effluent, divided by 0.26 m^2, which is the surface area of the sediment.

The phosphate releasing flux from the sediment is shown in Fig. 13. The fluxes increased in both GCA container and control. One of the possible reasons for the increasing flux is the decrease of sediment ORP. The phosphate release from the sediment is enhanced [19, 20] since ferric salts are reduced into ferrous salts and iron phosphate is released into the overlying water simultaneously under reduced conditions similar to the conditions in the present study. This observation is supported by the decreasing ORP values from -350 mV to -380- -440 mV owing to the decomposition of organic matter, etc. (Fig. 12). The phosphate releasing flux from the sediment into overlying water in the control was 110-540 μmol/m^2/d, which was slightly higher than that of Hiroshima Bay in a stratified period: -130-460 μmol/m^2/d [21]. On the other hand, the flux of the GCA container was 61-320 μmol/m^2/d. The phosphate releasing flux into overlying water from the sediment of the GCA container decreased 37-44% compared to the control.

The concentration of hydrogen sulfide in the pore water of the GCA container was <0.1-1.0 mg-S L^{-1} (Fig. 8). On the other hand, the hydrogen sulfide concentration of the control increased to 7.6 mg-S L^{-1} corresponding to the decrease in the DO concentration in the overlying water (Fig. 3) caused by the oxidation of hydrogen sulfide [22]. The decrease in concentration of hydrogen sulfide in the GCA container may have been caused by two processes below: (1) the GCA adsorbed hydrogen sulfide effectively by formation of FeS_2 and oxidation to sulfur [9]. (2) the deactivation of sulfate-reducing bacteria due to increase in pH exceeding their tolerable maxima at 8.5 as described above. Thus, the application of GCA is effective in reducing hydrogen sulfide in pore water and causes the suppression of DO consumption required for the oxidation of hydrogen sulfide.

Generally, the concentration of NH_4^+ in the GCA container was higher than the control by Day 25, which is caused by increasing sediment pH in the GCA container (Figs. 5, 11). Since the NH_4^+ adsorbed on the sediment electrostatically changes to NH_3 (ammonia) under a high pH, the ammonia without positive charge is released into the pore water [23, 24]. The increasing trend of NH_4^+ concentration in the overlying water of the GCA container during on Days 0-25 corresponded well with the sediment pH of the GCA container. Thereafter, on Days 35-45, concentration of NH_4^+ in the control was higher than that of GCA container, while concentration of NO_2^- and NO_3^- in the GCA container was higher than the control (Fig. 6). The percent ratio of DIN species in the overlying water is shown in Fig. 14. The ratio of NH_4^+ in the GCA container was higher than that of the control during Days 0-25 owing to the sediment pH increase described above, whereas the ratio of NO_3^- in the GCA container was higher than that of the control after Day 25. This may be due to a decrease in the nitrification rate in the control container because the DO concentration was lower in the control than the GCA container on Days 35-45.

Most of the dissolved nitrogen (DIN; total of dissolved NH_4^+, NO_2^- and NO_3^-) in the pore water were NH_4^+ form (Fig. 9, 10) because ORP of the sediment was so reductive at -436 to -328 mV that nitrification cannot be enhanced.

5. Conclusions

The purpose of the present study is to evaluate the remediation efficiency of GCA application to organically-enriched sediments in terms of reducing hydrogen sulfide and phosphate.

The results showed that GCA can reduce the concentration of PO_4^{3-} in the pore water effectively even though under highly reduced condition and consequently, reduced phosphate releasing flux from the sediment into the overlying water. The GCA application has a big advantage in terms of its being independent of sediment ORP, especially since in highly reductive sediments such iron type amendments cannot be applied.

The hydrogen sulfide in the pore water was also reduced with the application of GCA throughout the experimental periods due to adsorption and deactivation of sulfate reducing bacteria by increase in pH.

Based on the results obtained in this study, it can be concluded that the application of GCA to organically enriched sediments is effective in reducing phosphate releasing flux and concentration of hydrogen sulfide in pore water. The GCA, therefore, is a promising material for remediation of coastal sediments.

The results presented two-pronged environmental measures, namely, to use an industrial by-product safely on one hand, and its effective use as a non-polluting agent to improve deteriorating coastal sediment conditions on the other hand.

This proposed simple remediation technology involving the mixing of the GCA with the sediment also holds much promise for environmental restoration in many developing countries where expensive remediation technology is generally unavailable and impractical. Areas where pollution-causing coal thermal power plants are being operated will stand to benefit tremendously from this technology. The GCA used in this study is commercially sold, and usually used as a material for construction in Japan. It is not difficult to source enough amount of GCA for remediation of coastal sediments because some mass production plants for the materials are in operation. For example, according to one manufacturer, maximum daily output of GCA is 600 t per plant represents an average production. The proposed method in this study can be channeled for more effective environmental remediation efforts and at the same time eliminating costly disposal problems and promoting recycling consciousness and waste reduction within the society.

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Figure captions

Fig.1 Schematic drawing of the experimental setting.

Fig. 2 Change in pH of overlying water over time.
○: Control; 50 L of sediment only, ◆: Granulated coal ash; 50 L of sediment mixed with 50 L of Granulated coal ash, Bars represent standard deviation of triplicates.

Fig. 3 Change in DO concentrations of overlying water over time.
○: Control; 50 L of sediment only, ◆: Granulated coal ash; 50 L of sediment mixed with 50 L of Granulated coal ash, Bars represent standard deviation of triplicates.

Fig. 4 Change in PO_4^{3-} concentrations of overlying water over time.
○: Control; 50 L of sediment only, ◆: Granulated coal ash; 50 L of sediment mixed with 50 L of Granulated coal ash, Bars represent standard deviation of triplicates.

Fig. 5 Change in NH_4^+ concentrations of overlying water over time.
○: Control; 50 L of sediment only, ◆: Granulated coal ash; 50 L of sediment mixed with 50 L of Granulated coal ash, Bars represent standard deviation of triplicates.

Fig. 6 Change in NO_2^- and NO_3^- concentrations of overlying water over time.
○: Control; 50 L of sediment only, ◆: Granulated coal ash; 50 L of sediment mixed with 50 L of Granulated coal ash, Bars represent standard deviation of triplicates.

Fig. 7 Change in PO_4^{3-} concentrations of pore water over time.
○: Control; 50 L of sediment only, ◆: Granulated coal ash; 50 L of sediment mixed with 50 L of Granulated coal ash

Fig. 8 Change in H_2S-S concentrations of pore water over time.
○: Control; 50 L of sediment only, ◆: Granulated coal ash; 50 L of sediment mixed with 50 L of Granulated coal ash, Bars represent standard deviation

of triplicates.

Fig. 9 Change in NH_4^+ concentrations of pore water over time.
○: Control; 50 L of sediment only, ◆: Granulated coal ash; 50 L of sediment mixed with 50 L of Granulated coal ash

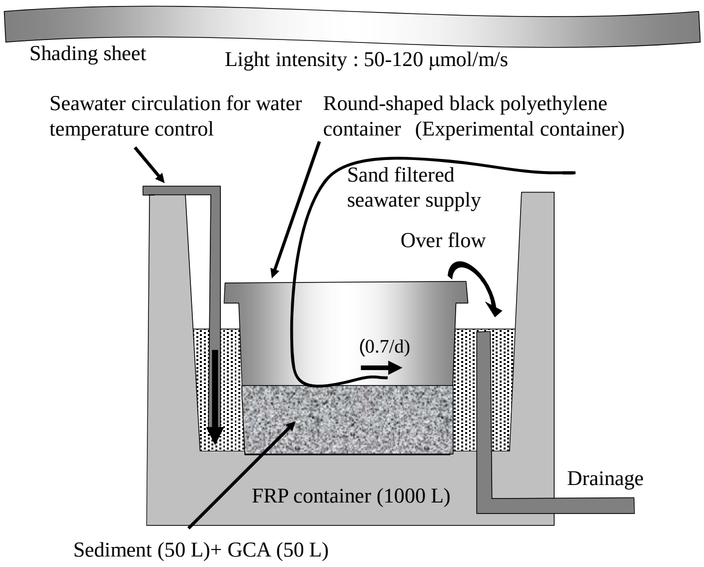
Fig. 10 Change in NO_2^- and NO_3^- concentrations of pore water over time.
○: Control; 50 L of sediment only, ◆: Granulated coal ash; 50 L of sediment mixed with 50 L of Granulated coal ash

Fig. 11 Change in sediment pH over time.
○: Control; 50 L of sediment only, ◆: Granulated coal ash; 50 L of sediment mixed with 50 L of Granulated coal ash, Bars represent standard deviation of triplicates.

Fig. 12 Change in sediment ORP over time.
○: Control; 50 L of sediment only, ◆: Granulated coal ash; 50 L of sediment mixed with 50 L of Granulated coal ash, Bars represent standard deviation of triplicates.

Fig. 13 PO_4^{3-} releasing fluxes from the sediment.
○: Control; 50 L of sediment only, ◆: Granulated coal ash; 50 L of sediment mixed with 50 L of Granulated coal ash

Fig. 14 The daily percent ratio of DIN species throughout the study period.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Light intensity : 50-120 µmol/m/s
Seawater circulation for water temperature control
Round-shaped black polyethylene container (Experimental container)
Sand filtered seawater supply
Over flow
(0.7/d)
Drainage
FRP container (1000 L)
Sediment (50 L)+ GCA (50 L)

Fig.1

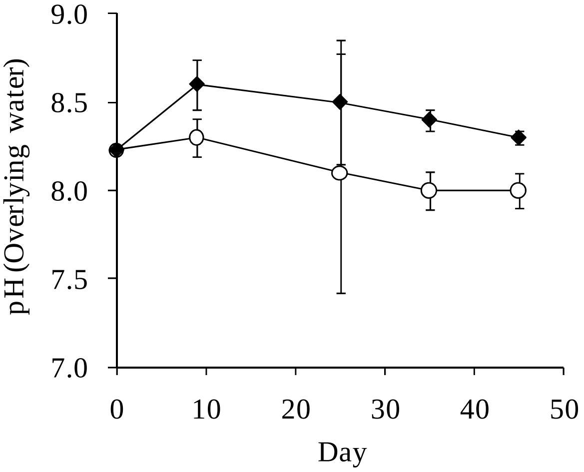

Fig. 2

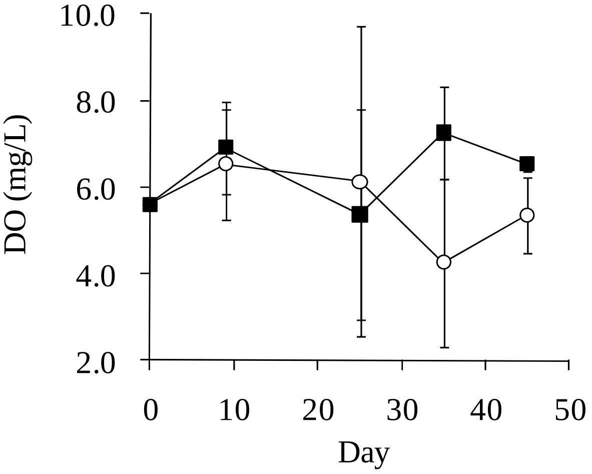

Fig. 3

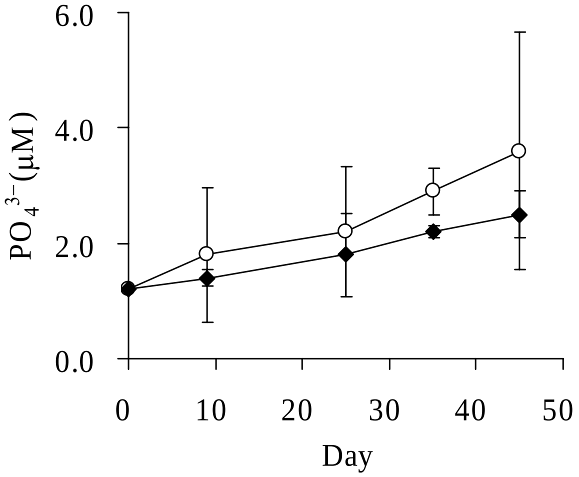

Fig. 4

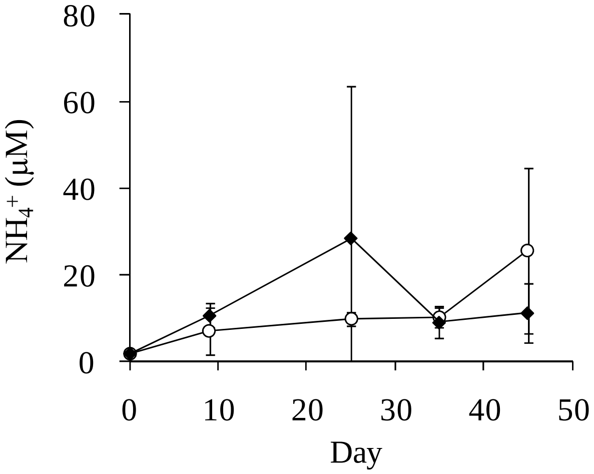

Fig. 5

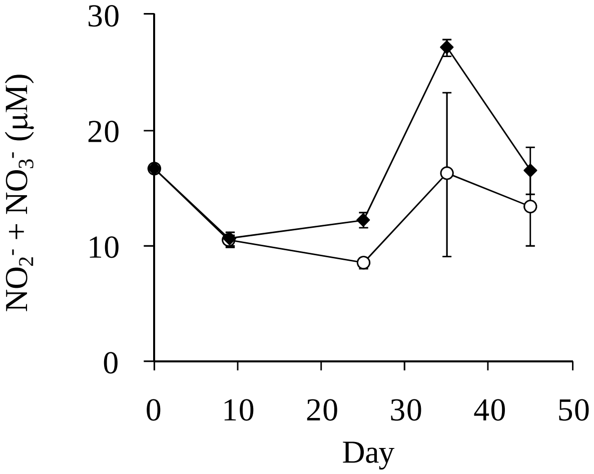

Fig. 6

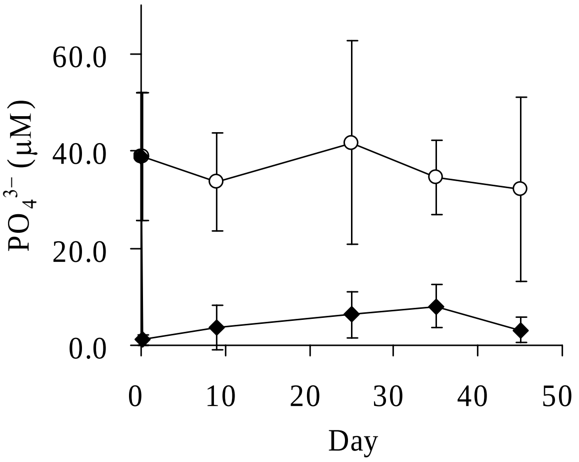

Fig. 7

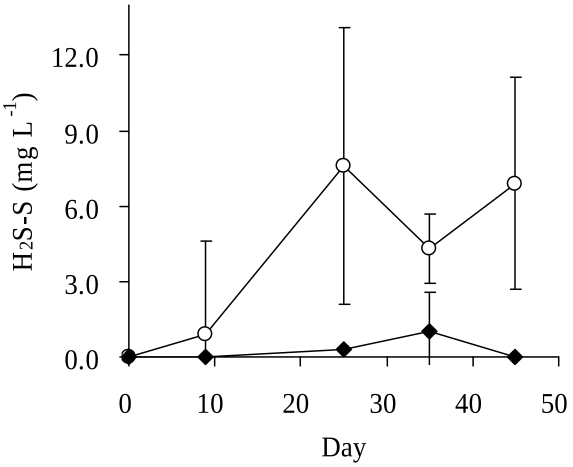

Fig. 8

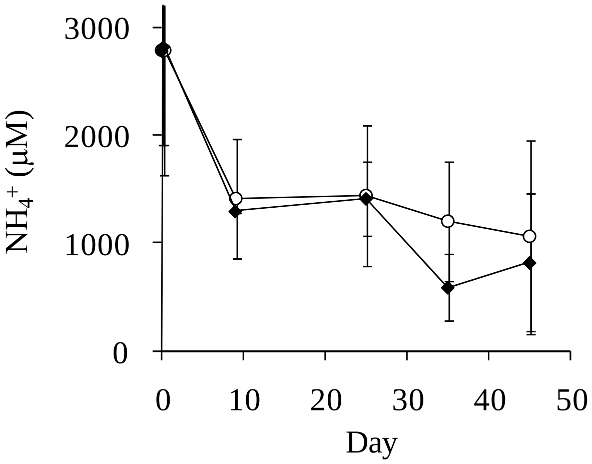

Fig. 9

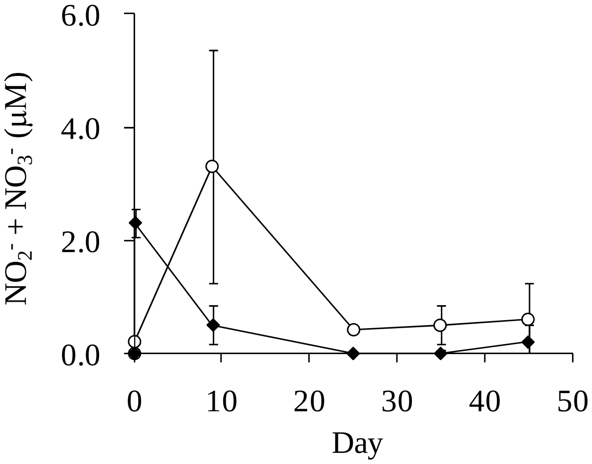

Fig. 10

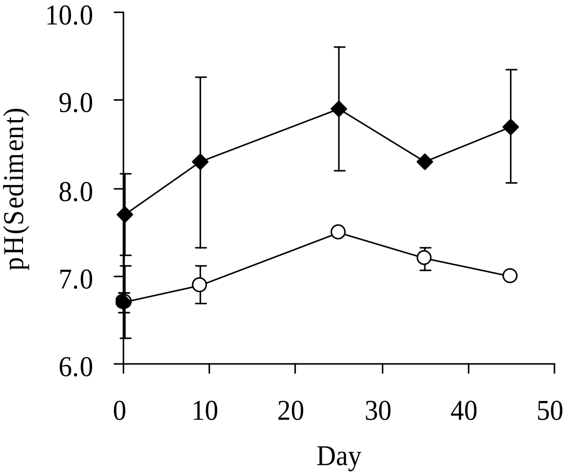

Fig. 11

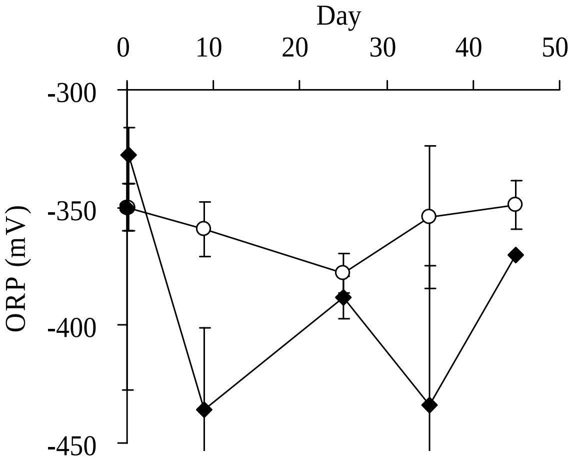

Fig. 12

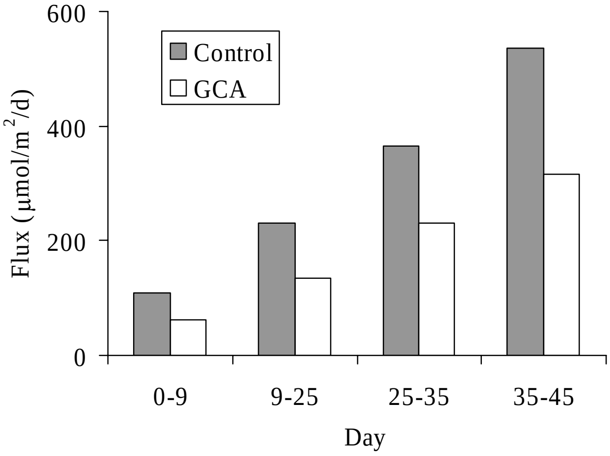

Fig. 13

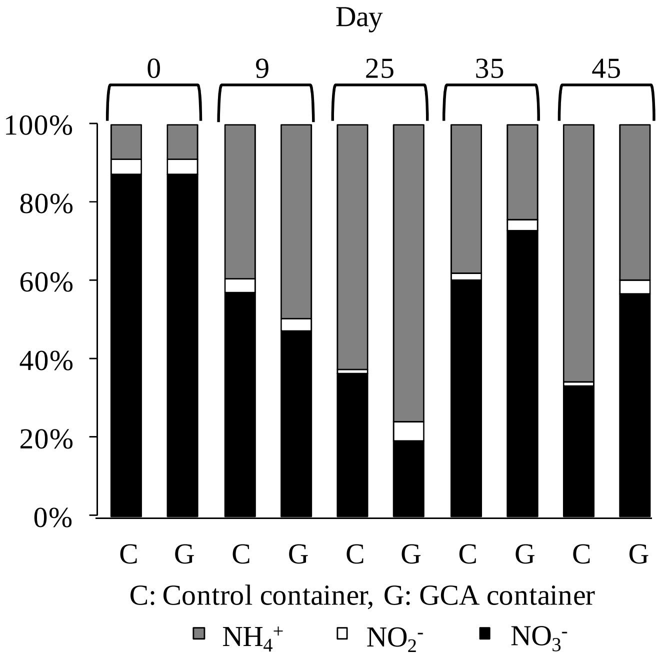
Day
0
9
25
35
45
100%
80%
60%
40%
20%
0%
C
G
C
G
C
G
C
G
C
G
C: Control container, G: GCA container
▨ NH_4^+
☐ NO_2^-
■ NO_3^-

Fig. 14