Estimation of hydrogen sulfide removal efficiency with granulated coal ash applied to eutrophic marine sediment using a simplified simulation model

Asaoka, Satoshi ; Yamamoto, Tamiji ; Yamamoto, Hironori ; Okamura, Hideo ; Hino, Kazutoshi ; Nakamoto, Kenji ; Saito, Tadashi

(Citation)
Marine Pollution Bulletin,94(1-2):55-61

(Issue Date)
2015-05-15

(Resource Type)
journal article

(Version)
Accepted Manuscript

Estimation of hydrogen sulfide removal efficiency with granulated coal ash applied to eutrophic marine sediment using a simplified simulation model

Satoshi ASAOKA1)*, Tamiji YAMAMOTO2), Hironori YAMAMOTO3), Hideo OKAMURA1), Kazutoshi HINO4), Kenji NAKAMOTO4), Tadashi SAITO4)

1) Research Center for Inland Seas, Kobe University
5-1-1 Fukaeminami, Higashinada, Kobe, Japan 658-0022

2) Graduate School of Biosphere Science, Hiroshima University
1-4-4 Kagamiyama, Higashi-Hiroshima, Japan 739-8528

3) FUKKEN Co. Ltd.
2-10-11 Hikari, Higashi-ku, Hiroshima-shi, Hiroshima, Japan 732-0052

4) The Chugoku Electric Power Co., Inc.
4-33, Komachi,Naka-ku,Hiroshima-shi,Hiroshima, Japan 730-8701

*Corresponding author:
Tel & Fax: +81-78-431-6357, E-mail: s-asaoka@maritime.kobe-u.ac.jp
Address: Research Center for Inland Seas, Kobe University, 5-1-1 Fukaeminami, Higashinada, Kobe, Japan 658-0022

Abstract

Hydrogen sulfide generated in eutrophic marine sediment is harmful for living organisms. It is therefore necessary to remove hydrogen sulfide from the sediment to restore benthic ecosystems. Previous studies revealed that granulated coal ash, which is a by-product of coal thermal electric power stations, could remove and oxidize hydrogen sulfide. In this study, we propose a simplified simulation model to estimate the hydrogen sulfide removal efficiency of granulated coal ash. Hydrogen sulfide concentrations in eutrophic marine sediment pore water with and without the application of granulated coal ash were calculated by the proposed model, and the outputs were compared with semi-field or field observation data. The model outputs reproduced the observed data well. Using the proposed model outputs, we suggest an optimum application dosage of granulated coal ash for remediating eutrophic marine sediment.

Key words

eutrophication, hypoxia, sediment, remediation, model

1. Introduction

Hydrogen sulfide is one of the serious environmental issues in enclosed water bodies. Nutrient dissolution from eutrophic sediments, together with excessive terrigenous material loads, trigger massive algae growth in such water bodies. Oxidative decomposition of organic matter, including dead algal cells, consumes dissolved oxygen in the water column, which may induce hypoxic water mass in warm stratified seasons. Under such anoxic conditions, hydrogen sulfide is produced through sulfate reduction in the interstitial water by sulfate-reducing bacteria using sedimentary organic matter as a reducing agent and energy source (Berner, 1984).

Hydrogen sulfide is detected in high concentrations in eutrophic enclosed water bodies (Reese et al., 2008; Yamamoto et al., 2012; Asaoka et al., 2012a; Sakai et al., 2013). Hydrogen sulfide is harmful for living organisms because it interferes with cytochrome c oxidase, the last enzyme of the electron transport system (Affonso et al., 2004). As a result, viability of benthic organisms and demersal fish might decrease due to its high toxicity. Therefore, it is very important to remove hydrogen sulfide from deteriorated sediments of enclosed water bodies in order to restore the ecosystems.

Several environmental remediation agents have been developed to remove hydrogen sulfide from eutrophic marine sediments, including granulated coal ash, crushed oyster shells and steel slags (Asaoka et al., 2009a; Asaoka et al., 2012b; Kim et al., 2012; Asaoka et al., 2013; Asaoka et al., 2014). In this study, we focused on granulated coal ash (GCA) because of its high adsorption capacity (108 mg S g^{-1}) for hydrogen sulfide (Asaoka et al., 2009b). Moreover, it was revealed by an experimental study that the adsorption sites for hydrogen sulfide on GCA are partially regenerated by oxygen (Asaoka et al., 2014). Field and semi-field trials have also been conducted using the materials (Asaoka et al., 2009c; Yamamoto et al., 2013; Kim et al., 2014). In the semi-field experiment, application of GCA significantly decreased the concentration of hydrogen sulfide in the pore water by 77–100% compared to the control (Asaoka et al., 2009c). Field experiments carried out in Hiroshima Bay, a semi-enclosed bay located in the western Seto Inland Sea of Japan, showed the concentration of hydrogen sulfide in the sediments where the GCA was applied was maintained at almost zero, whereas it ranged from 0.1–2.4 mg S L^{-1} in control sites (Kim et al., 2014). Although the application of GCA to eutrophic marine sediment is effective in removing hydrogen sulfide, the application dosage of GCA has not been fully optimized. The purpose of this study was to optimize application dosage of GCA to eutrophic marine sediments using the proposed simplified simulation model for estimating hydrogen sulfide removal efficiency.

2. Materials and methods

2.1. Granulated coal ash

GCA is produced through the granulation of coal fly ash from coal thermal electric power stations (Chugoku Electric Power). The process involves adding cement as a binder to a ratio of approximately 15% of the final product. GCA is mainly composed of SiO_2, CO_3, Al_2O_3, CaO, organic carbon, and Fe_2O_3 with quartz and aluminosilicate crystal phase, in concentrations of 395, 133, 126, 55.4, 27.4, and 22.5 g kg^{-1}, respectively (Asaoka et al., 2012b). The environmentally regulated substances dissolved from the GCA used in this study were obviously below the standard levels for environmental criteria in Japan (Asaoka et al., 2008).

2.2 Simulation on semi-field experiments

Observed data used in this study were collected by semi-field experiments. The data have been partially published (Asaoka et al., 2009c). The semi-field experiments were designed to simulate the innermost area of Hiroshima Bay, one of the enclosed water bodies near a big metropolis (Hiroshima City) in Japan. Sixty kg of sediments were collected from the Ohko Inlet (34° - 21' 51"N, 132° - 28' 39"E) or Ohzu Inlet (34° - 23' 17"N, 132° - 29' 52"E) located at the head of Hiroshima Bay (Fig. 1). The Ohko Inlet is affected by inflow from eutrophic Kaita Bay next to the inlet and by settling fluxes from dead algal cells (Asaoka and Yamamoto, 2011); the Ohzu Inlet is affected by domestic wastewater from Hiroshima City. Sediments were mixed in round black polyethylene containers (550 mm in diameter, 420 mm in height; Fig. 2). The wet weight ratios of the GCA (5 mm in diameter) and inlet sediments were 13:60 for the Ohko Inlet and 50:60 for the Ohzu Inlet, respectively.

Sand-filtered natural seawater was supplied and allowed to overflow at an exchange rate of 0.7 d^{-1}. These containers were placed in a water bath (1000 L FRP container) to prevent rapid water temperature changes throughout the experimental period. In the case of the experiment using the Ohzu Inlet sediments, the light intensity was adjusted from 50–120 μmol m^{-2} s^{-1} to simulate the conditions of shallow coastal areas using loosely woven nylon black sheets (cheese cloth) placed over the containers. Overlying water temperature ranged 20.8 to 25.5 °C for the Ohko Inlet and 23.6 to 29.4 °C for the Ohzu Inlet, respectively. Sediment without the GCA application was used as a control. The container experiment was conducted in triplicate.

Sediment pore water was collected by centrifugation of the sediment sample at 3,500 rpm for 10 min, and used for determining concentration of hydrogen sulfide with a detection tube (200SA and 200SB, Komyo Rikagaku

Kougyo). Other analytical parameters such as pH, ORP, salinity, dissolved oxygen and nutrients were described in Asaoka et al. (2009c).

2.3 Simulation of field experiment

Data from the field experiment used in this model was collected from Ohko Inlet (locations; 34^{o} - 21' 51"N, 132^{o} - 28' 39"E; 0.047 km^2, 4 m avg. depth) at the innermost area of Hiroshima Bay, Japan, which is affected by terrigenous load (Fig. 1; Asaoka and Yamamoto, 2011). The GCA (10-20 cm diameter) stuffed in a net bag (mesh size: 5 mm) was installed to cover $4m^2$ of muddy sediments to a depth of 20 cm in July 2010. Overlying water temperature ranged 24 to 29 ^{o}C. The control site did not receive any treatment. Sediment pore water was collected with a syringe by divers. The concentration of hydrogen sulfide was determined on the basis of JIS K 0102(2013). The average porosity of the GCA applied in the field experiment was 39%. Therefore, the mixture ratio of the GCA to wet sediment was set to 39:61 in this model.

2.4. Model framework

The framework of the model developed in the present study was designed to express sulfur cycles in the sediments, as shown in Fig. 3. Hydrogen sulfide (H_2S-S) in the sediment pore water was generated through sulfate reduction by sulfate-reducing bacteria. Hydrogen sulfide was oxidized to oxidized sulfur species (Ox. S), such as elemental sulfur, thiosulfate and sulfate by consuming oxygen in the overlying water. When GCA is applied to sediments, hydrogen sulfide may diffuse to the GCA following the concentration gradient. Accordingly, hydrogen sulfide is adsorbed onto the GCA and oxidized to sulfur.

2.5. Parameters and equations used in this study

Parameters used in this study are summarized in Table 1. Diffusion rate of hydrogen sulfide to the GCA (mg d^{-1}) was calculated by equation (1).

$$DF[H_2S] = D \cdot \frac{(C_p - C_{coal}) \cdot S_{coal}}{L/2 \cdot R} \cdot W, \tag{1}$$

where $DF[H_2S]$ is the diffusion rate of hydrogen sulfide (mg d^{-1}); D is the molecular diffusion coefficient (m^2 d^{-1}); C_p is the concentration of hydrogen sulfide in pore water (mg m^{-3}); C_{coal} is the concentration of hydrogen sulfide on the surface of the GCA (mg m^{-3}); S_{coal} is the specific surface area of the GCA (m^2 g^{-1}); L is the interparticle distance of the GCA (m); W is the application dosage of the GCA (g); and R is the retardation coefficient (-).

C_{coal} was calculated from equation (2).

$$C_{coal} = C_p - C_p \cdot K \quad (if\ C_{coal} < 0\ then\ 0\ else\ C_{coal}), \tag{2}$$

where K is the removal rate of hydrogen sulfide by the GCA (d^{-1})

L was calculated from equation (3)

$$L = 2(r_m - r), \tag{3}$$

where r_m is the radius of the sediment and the GCA mixture (m) calculated from equations (4 and 5), and r is radius of the GCA (m).

$$V = \frac{4}{3}\pi \cdot r^3 \cdot \frac{[Coal] + [Sed]}{[Coal]} \tag{4}$$

$$r_m = \sqrt[3]{\frac{3V}{4\pi}} \qquad (5)$$

where V is the volume of sediment and the GCA mixture (m^3) calculated by equation (4); r is the radius of the GCA (m); $[Coal]$ is the volume of applied GCA (m^3); and $[Sed]$ is the volume of sediment (m^3).

The amount of hydrogen sulfide in sediment pore water was calculated by equation (6).

$$\frac{d[H_2S]}{dt} = VF[H_2S] \pm DF[H_2S] - AF[H_2S], \qquad (6)$$

where $[H_2S]$ is the amount of hydrogen sulfide in sediment pore water (mg); VF$[H_2S]$ is the generation rate of hydrogen sulfide (mg d^{-1}); DF$[H_2S]$ is the diffusion rate of hydrogen sulfide (mg d^{-1}) calculated by equation (1); and AF$[H_2S]$ is the oxidation rate of hydrogen sulfide (mg d^{-1}).

VF[H_2S] was calculated by equation (7).

$$\mathrm{VF}[H_2S] = T \cdot K_{red} \cdot C_d \cdot W_d \cdot V_{p,} \qquad (7)$$

where T is the coefficient of temperature effect (-); K_{red} is the reduction rate of sulfate by sulfate-reducing bacteria (mg L^{-1} $cell^{-1}$ d^{-1}); C_d is the cell density of sulfate-reducing bacteria in the marine sediment (cells g^{-1} dry weight); W_d is the dry weight of the sediment (g); and V_p is the volume of sediment pore water (L). The cell density of sulfate-reducing bacteria was tuned according to Asaoka et al. (2009d).

T was calculated from equation (8) following Canfield et al. (2006).

$$\mathrm{T} = 0.0008 \cdot t_w^2 + 0.0054 \cdot t_w \ (10 \leq t_w \leq 35), \qquad (8)$$

where t_w is the overlying water temperature. The assigned overlying water temperature was the observed value.

AF[H_2S] was calculated from equation (9).

$$\mathrm{AF}[H_2S] = K_{ox} \cdot C \cdot V_p, \qquad (9)$$

where K_{ox} is the oxidation rate of hydrogen sulfide (d^{-1}); C is the concentration of hydrogen sulfide in pore water (mg L^{-1}); and V_p is the volume of sediment pore water (L).

K_{ox} was empirically calculated from equation (10) according to Asaoka et al. (2012a)

$$K_{ox} = -0.0131C + 0.4272 \ (0 < K_{ox}) \qquad (10)$$

STELLA (ver. 9.0.3; isee systems, Inc.) was used for the calculations. The initial value of hydrogen sulfide in the pore water was calculated from its initial concentration in this water. The proposed sulfur flow model was employed with time step 0.01 day. Sensitivity analyses conducted while application dosage of the GCA were changed in the range of 0–50 kg.

3. Results and discussion

3.1 Simulation of semi-field experiments

3.1.1 Simulation of hydrogen sulfide in sediment pore water

Simulated control (without GCA application) and GCA application output in the Ohko and Ohzu Inlets mostly corresponded with observed values (Figs. 4 and 5). However, in the case of the Ohko Inlet, the model output for H_2S-S in GCA was underestimated at Day 18 compared to the observed value (Fig. 4). One possible reason for the error is that the water temperature went up sharply to 25 °C on that day, so that the observed sulfate-reducing rate was higher than the simulated value. Meanwhile, the model output for H_2S-S in the control of Ohzu Inlet was overestimated at Day 9 compared to the observed value (Fig. 5). The observed sulfate-reducing rate might have been low compared to the simulated value because the sulfate-reducing bacteria might not have been acclimatized within 9 days. When this model is applied to other sediments, hydrogen sulfide concentration in pore water and water or sediment temperature should be measured to validate the model output of sulfate-reducing rate.

3.1.2 Calculated sulfur flow with and without GCA application

Calculated daily average of sulfur flow in Ohko Inlet sediment (wet weight base) throughout the experimental period is shown in Fig. 6. Model output showed 2.4 mg kg^{-1} d^{-1} of sulfur was generated as hydrogen sulfide (H_2S-S) from sulfate by sulfate-reducing bacteria activities. In the case of the control, 2.0 mg kg^{-1} d^{-1} of sulfur from hydrogen sulfide was oxidized. On the other hand, in the case of applied GCA, the amount of hydrogen sulfide oxidation decreased to 1.4 mg kg^{-1} d^{-1}, down 30% from the control; this was attributed to 0.87 mg kg^{-1} d^{-1} of sulfur from hydrogen sulfide being adsorbed onto the GCA and oxidized.

In the case of the Ohzu Inlet sediment, 0.65 mg kg^{-1} d^{-1} of sulfur was generated as hydrogen sulfide (H_2S-S) from sulfate, and 0.6 mg kg^{-1} d^{-1} of sulfur from hydrogen sulfide was oxidized (Fig. 7). In the case of applied GCA, the amount of hydrogen sulfide oxidation decreased to 0.044 mg kg^{-1} d^{-1}, down 92.7% from the control. Accordingly, 0.59 mg kg^{-1} d^{-1} of sulfur from hydrogen sulfide was adsorbed onto the GCA and oxidized.

3.1.3 Effect of the GCA application dosage on hydrogen sulfide concentration in sediment pore water

Sensitivity analyses were carried out to estimate hydrogen sulfide concentration in the Ohko and Ohzu Inlets' sediment pore water under various GCA application dosages (Figs. 8 and 9). In this model, hydrogen sulfide concentration in the sediment pore water did not reach a steady state, because the generation rate of hydrogen sulfide was controlled by temperature. Therefore, we discuss the hydrogen sulfide concentration in the sediment pore water using average values. In the case of the Ohko Inlet, the average concentration of hydrogen sulfide in the sediment pore water throughout the container experiment period was 10.2, 6.4, 3.9, 2.5, 1.7 and 1.2 mg-S L^{-1} for the control, with 10, 20, 30, 40 and 50 kg of the GCA application per 60 kg of sediment, respectively (Fig. 8).

In the case of the Ohzu Inlet, the average concentration of hydrogen sulfide in the sediment pore water throughout the container experiment period was 5.9, 2.8, 1.4, 0.80, 0.51 and 0.35 mg-S L^{-1} for the control, with 10, 20, 30, 40 and 50 kg of GCA application per 60 kg of sediment, respectively (Fig. 9). Given that hydrogen sulfide exerts a negative impact on aquatic organisms even at low concentrations of 0.09-1.9 mg-S L^{-1} (Marumo and Yokota, 2012), more than 40 or 20 kg of GCA application for Ohko and Ohzu Inlets, respectively, would be suitable for suppressing hydrogen sulfide concentration in pore water at less than 1.9 mg L^{-1}.

3.1.4 Effect the GCA application dosage on oxygen demand for hydrogen sulfide oxidation

As mentioned above, hypoxic water formation is a serious issue in enclosed water bodies. Oxygen consumption by the sediment can be categorized into two major fractions: chemical and biological. It has been reported that chemical oxygen consumption in Hiroshima Bay accounts for 23.3–105% of the sediment oxygen demands (Seiki et al., 1994). Therefore, the chemical oxygen consumption of sediments is one of the significant factors in hypoxic water formed there. The proposed model focuses on chemical oxygen consumption only through hydrogen sulfide oxidation. (Simulation of dissolved oxygen in overlaying water is excluded.)

Sulfide oxidation can be expressed as equations (11)–(13) (Chen and Morris, 1972).

$$2HS^- + O_2 + 2H^+ \rightarrow 2H_2O + 2S \qquad (11)$$

$$2HS^- + 2O_2 \rightarrow H_2O + S_2O_3^{2-} \qquad (12)$$

$$2HS^- + 4O_2 \rightarrow 2SO_4^{2-} + 2H^+ \qquad (13)$$

Overall oxygen consumption attributed to hydrogen sulfide oxidation was estimated from equations (11)–(13) as follows. First, it is known that 7 mol of O_2 stoichiometrically require 6 mol of HS^- for oxidation. The cumulative oxygen consumption throughout the experimental periods was stoichiometrically estimated, as shown in Figs. 10 and 11. In the case of the

Ohko Inlet, 3,636 mg of oxygen was consumed by sulfide oxidation at the control throughout the experimental periods (Fig. 10). When GCA was applied to the sediment collected from the Ohko Inlet, oxygen consumption decreased significantly with increasing application dosage of GCA, because the GCA adsorbed and oxidized the hydrogen sulfide. Incidentally, the oxidation of hydrogen sulfide by the GCA does not necessarily involve oxygen (Asaoka et al., 2012b). For Ohzu Inlet, 1,921 mg of oxygen were consumed by sulfide oxidation at the control throughout the experiment periods (Fig. 11). On the other hand, for example, cumulative oxygen consumption was reduced 92.7% compared to the control when the GCA application dosage was 50 kg. Therefore, application of the GCA to sediments is effective in decreasing sediment oxygen demand by sulfide oxidation, as well as cutting down hydrogen sulfide concentration in sediment pore water.

3.2 Simulation of field experiment

Simulated control (without GCA application) and GCA application outputs coincided well with observed values (Fig. 12).

Calculated daily average of sulfur flow in sediment (wet weight base) throughout the experimental period is shown in Fig. 13. Model output showed 3.1 mg kg^{-1} d^{-1} of sulfur was generated as hydrogen sulfide (H_2S-S) from sulfate by sulfate-reducing bacteria activities. In the case of the control, 2.5 mg kg^{-1} d^{-1} of sulfur from hydrogen sulfide was oxidized. On the other hand, in the GCA applied sediment, hydrogen sulfide oxidation decreased to 0.42 mg kg^{-1} d^{-1}, down 83.2% from the control; 2.7 mg kg^{-1} d^{-1} of sulfur from hydrogen sulfide was adsorbed onto and oxidized by the GCA. Accordingly, the daily average of oxygen consumption required for hydrogen sulfur oxidation decreased to 0.49 mg kg^{-1} d^{-1} from 2.9 mg kg^{-1} d^{-1}.

4. Conclusions

The application dosage of GCA was successfully optimized to remove hydrogen sulfide in sediment pore water at less than 1.9 mg L^{-1} using the proposed model. The model output showed that more than 40 or 20 kg of the GCA application were required for Ohko and Ohzu Inlets sediments, respectively, per 60 kg. Accordingly, oxygen consumption required for hydrogen sulfide oxidation was lowered 76% and 72%, respectively, compared to non-GCA application. The proposed model in this study is effective in estimating optimum application dosage of GCA to remediate eutrophic marine sediment.

Acknowledgments

This study was conducted by in collaboration with The Chugoku Electric Power Co., Inc.

References

Affonso E.G., Polez V.L.P., Corrêa C.F., Mazon A.F., Araújo M.R.R., Moraes G., Rantin F.T. 2004. Physiological responses to sulfide toxicity by the air-breathing catfish, Hoplosternum littorale (Siluriformes, Callichthyidae), Comp. Biochem. Physiol. C 139 , 251-257.

Asaoka S., Yamamoto T., Yamamoto K. 2008. A preliminary study of coastal sediment amendment with granulated coal ash – Nutrient elution test and experiment on *Skeletonema costatum* growth-. J. Jpn. Water Environ, 31, 455-462 (Japanese with English abstract).

Asaoka S., Yamamoto T., Kondo S., Hayakawa S.2009a. Removal of hydrogen sulfide using crushed oyster shell from pore water to remediate organically enriched coastal marine sediments. Bioresour. Technol., 100, 4127-4132.

Asaoka S., Yamamoto T., Hayakawa S. 2009b. Removal of hydrogen sulfide using granulated coal ash. J. Jpn. Soc. Water Environ., 32, 363-368 (Japanese with English abstract).

Asaoka S., Yamamoto T., Yoshioka I., Tanaka H. 2009c. Remediation of coastal marine sediments using granulated coal ash. J. Hazard. Mater. 172, 92-98.

Asaoka S., Yamamoto K., Haraguchi K., Yamaoto T.. 2009d. Effects of granulated coal ash as a sediment amendment on benthic microalgae and microbial communities in the sediment, J Water Waste 51, 237-244 (in Japanese).

Asaoka S., Yamamoto T. 2011. Phosphorus mass balance in a highly eutrophic semi-enclosed inlet near a big metropolis: A small inlet can contribute towards particulate organic matter production, Mar. Pollut. Bull. 63, 237-242.

Asaoka S., Yamamoto T., Takahashi Y., Yamamoto H., Kim K.H., Orimoto K. 2012a Development of an on-site simplified determination method for hydrogen sulfide in marine sediment pore water using a shipboard ion electrode with consideration of hydrogen sulfide oxidation rate. Interdiscip. Stud. Environ. Chem. Environ. Pollut. Ecotoxicol. 6, 345-352.

Asaoka S., Hayakawa S., Kim K.H., Takeda K., Katayama M., Yamamoto T. 2012b.Combined adsorption and oxidation mechanisms of hydrogen sulfide on granulated coal ash. J. Colloid Interf. Sci., 377, 284-290.

Asaoka S., Okamura H., Morisawa R., Murakami H., Fukushi K., Okajima T., Katayama M., Inada S., Yogi C., Ohta T. 2013. Removal of hydrogen sulfide using carbonated steel slag. Chem. Eng. J. 228, 843-849.

Asaoka S., Okamura H., Akita Y., Nakano K., Nakamoto K., Hino K., Saito T., Hayakawa S., Katayama M., Inada Y. 2014. Regeneration of manganese oxide as adsorption sites for hydrogen sulfide on granulated coal ash. Chem. Eng. J. 254, 531-537.

Barnes, R.A. 1984. Sedimentary pyrite formation: An update. Geochim. Cosmochm. Acta 48, 605-615.

Canfield D.E., Olesen C.A., Cox R.P. 2006. Temperature and its control of isotope fractionation by a sulfate-reducing bacterium. Geochim. Cosmochim. Ac. 70, 548-561.

Chen K.Y., Morris J.C. 1972. Kinetics of oxidation of aqueous sulfide by O_2. Environ. Sci. Technol. 6, 529-537.

Japanese Standards Association, JIS K 0102(2013)136 39 Sulfide ion

Kim K.H., Asaoka S., Yamamoto T., Hayakawa S., Takeda K., Katayama M., Onoue T.2012.Mechanisms of hydrogen sulfide removal with steel making slag. Environ. Sci. Technol., 46, 10169-10174.

Kim K.H., Hibino T., Yamamoto T., Hayakawa S., Mito Y., Kenji N., Lee I.C. 2014. Field experiments on remediation of coastal sediments using granulated coal ash. Mar Pollut. Bull. 83, 132-137.

Li Y. H, Grogory S. 1974. Diffusion of ions in sea water and in deep-sea sedoments. Geochim. Cosmochim. Ac. 38, 703-714.

Marumo K, Yokota M. 2012. Review on aoshio and biological effects of hydrogen sulfide. Rep. Mar. Ecol. Res. Inst. 15, 23-40 (in Japanese).

Reese B.K., Anderson M.A., Amrhein C. 2008. Hydrogen sulfide production and volatilization in a polymictic eutrophic saline lake, Salton Sea, California. Sci.Total Environ. 406, 205-218.

Sakai S., Nakaya M., Sampei Y., Dettman D.L., Takayasu K. 2013. Hydrogen sulfide and organic carbon at the sediment–water interface in coastal brackish Lake Nakaumi, SW Japan. Environ. Earth. Sci. 68, 1999-2006.

Seiki T., Izawa H., Date E., Sunahara H. 1994. Sediment oxygen demand in Hiroshima bay. War. Res. 28, 385-393.

Yamamoto T., Kondo S., Kim K.H., Asaoka S., Yamamoto H., Tokuoka M., Hibino T. 2012. Remediation of muddy tidal flat sediments using hot air-dried crushed oyster shells. Mar. Pollut. Bull. 64, 2428-2434.

Yamamoto T., Harada K., Kim K.H., Asaoka S., Yoshioka I. 2013. Suppression of phosphate release from coastal sediments using granulated coal ash. Estuar. Coast. Shelf Sci. 116, 41-49.

Figures and Captions

Fig. 1 Location map of Ohko and Ohzu Inlets

Fig. 2 Schematic diagram of a semi-field experiment set up

Fig. 3 A model framework expressing sulfur flow designed in this study

Fig. 4 Simulated and observed hydrogen sulfide concentration in sediment pore water at Ohko Inlet

Fig. 5 Simulated and observed hydrogen sulfide concentration in sediment pore water at Ohzu Inlet

Fig. 6 Calculated daily average of sulfur flow in Ohko Inlet sediment

The value given in parentheses shows calculated daily average of sulfur flow in control or granulated coal ash applied containers.

Fig. 7 Calculated daily average of sulfur flow in Ohzu Inlet sediment

The value given in parentheses shows calculated daily average of sulfur flow in control or granulated coal ash applied containers.

Fig. 8 Calculated concentration of hydrogen sulfide in sediment pore water with various the granulated coal ash application dosage at Ohko Inlet

Fig. 9 Calculated concentration of hydrogen sulfide in sediment pore water with various the granulated coal ash application dosage at Ohzu Inlet

Fig. 10 Cumulative oxygen consumption of Ohko Inlet throughout the experimental periods

Fig. 11 Cumulative oxygen consumption of Ohzu Inlet throughout the experimental periods

Fig. 12 Simulated and observed hydrogen sulfide concentration in sediment pore water of the field experiment

Fig. 13 Calculated daily sulfur flow of the field experiment

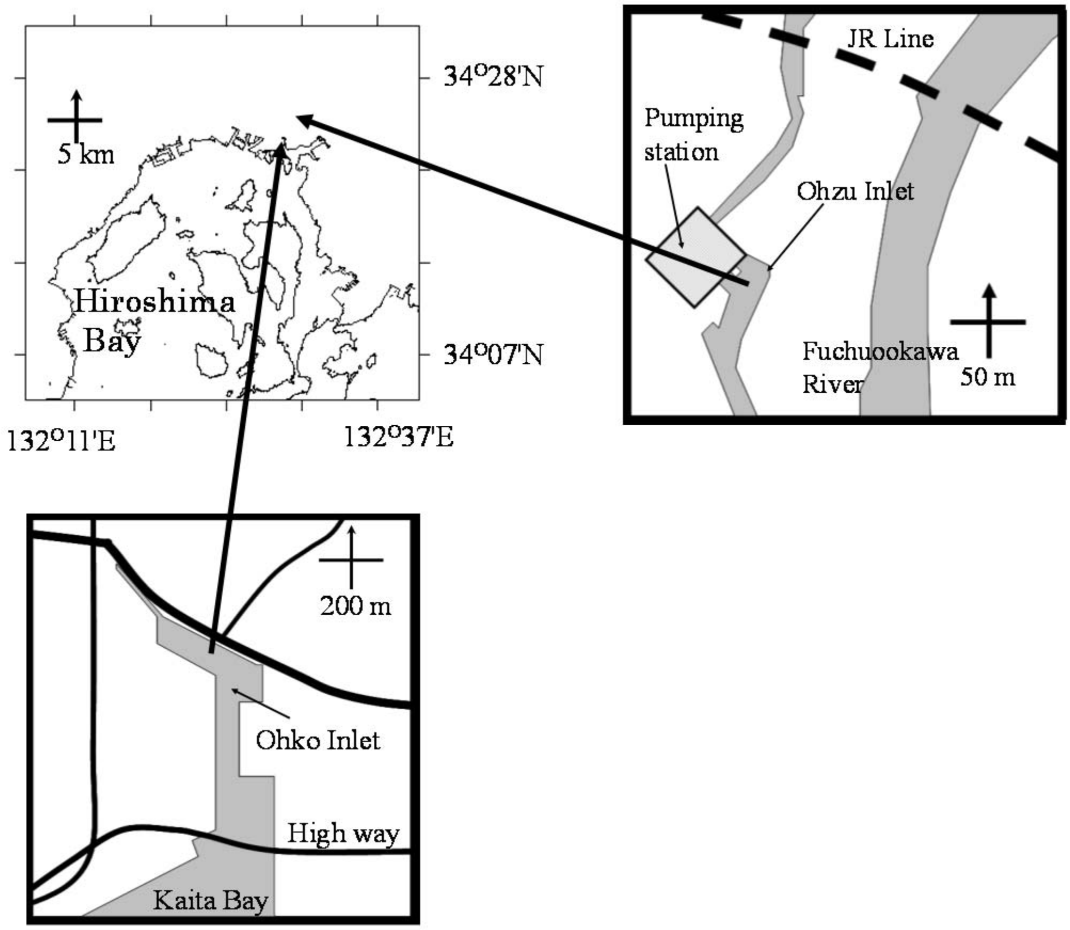


Fig. 1 Location map of Ohko and Ohzu Inlets

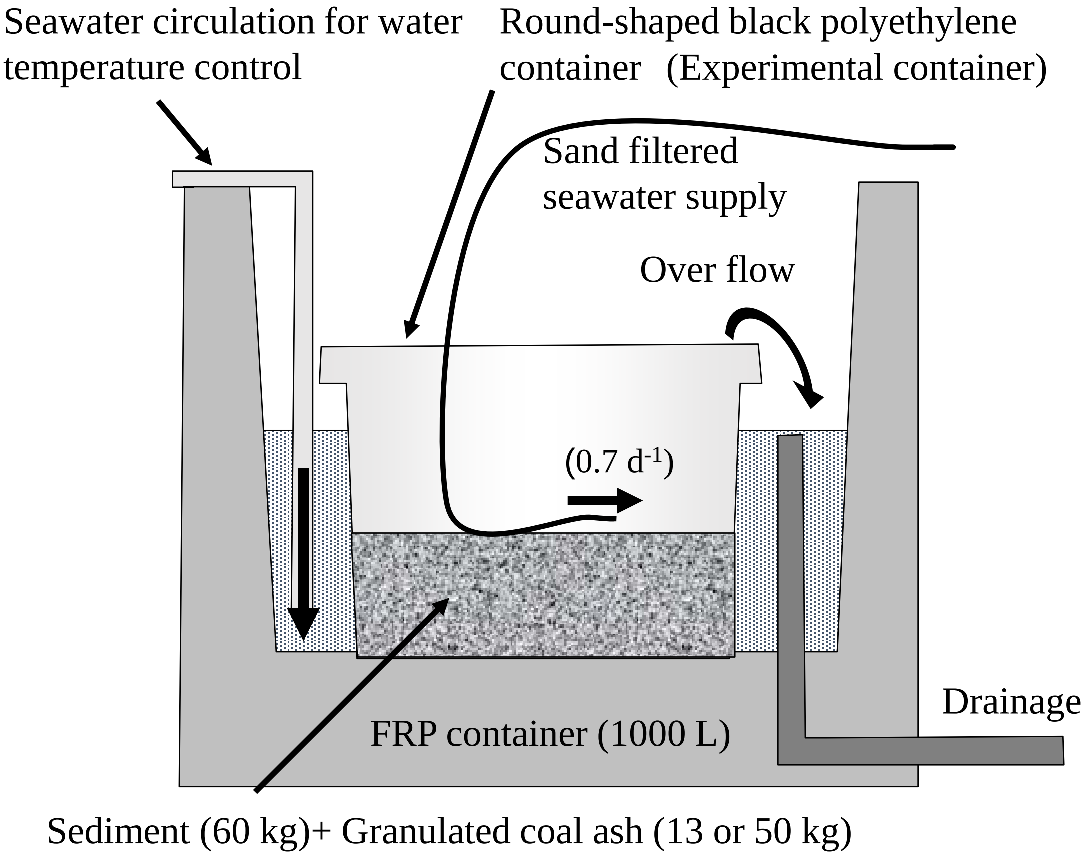


Fig. 2 Schematic diagram of a semi-field experiment set up

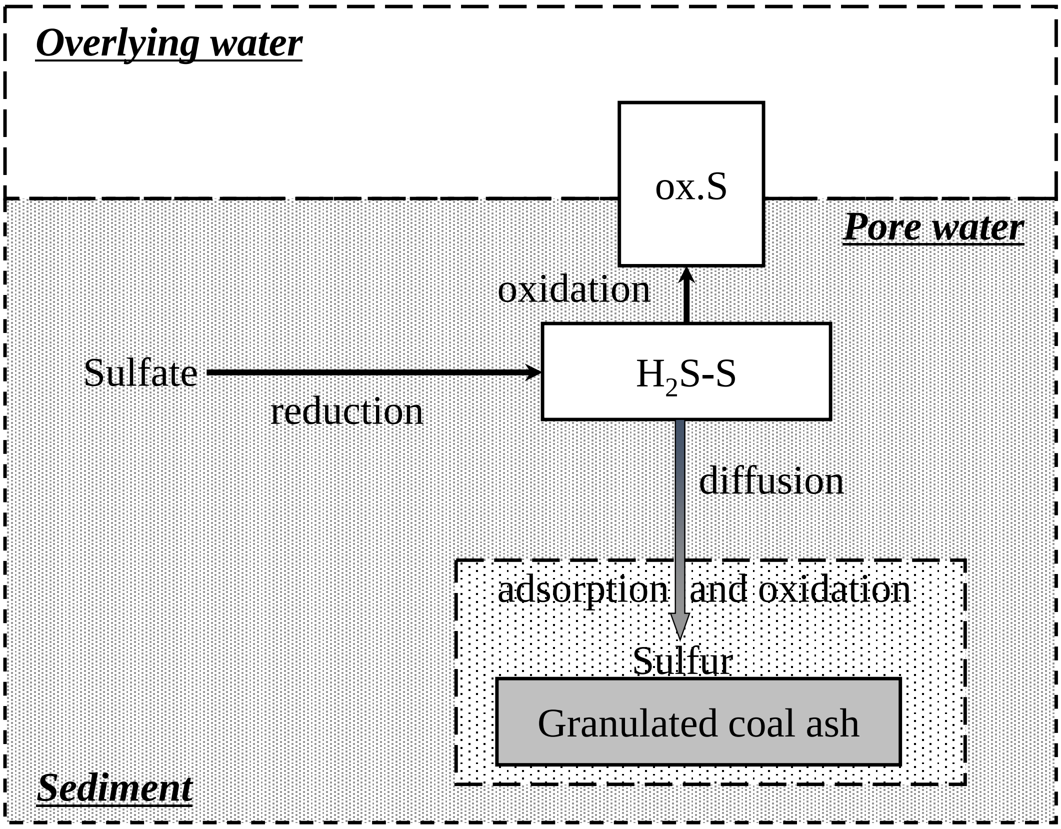


Fig. 3　A model framework expressing sulfur flow designed in this study

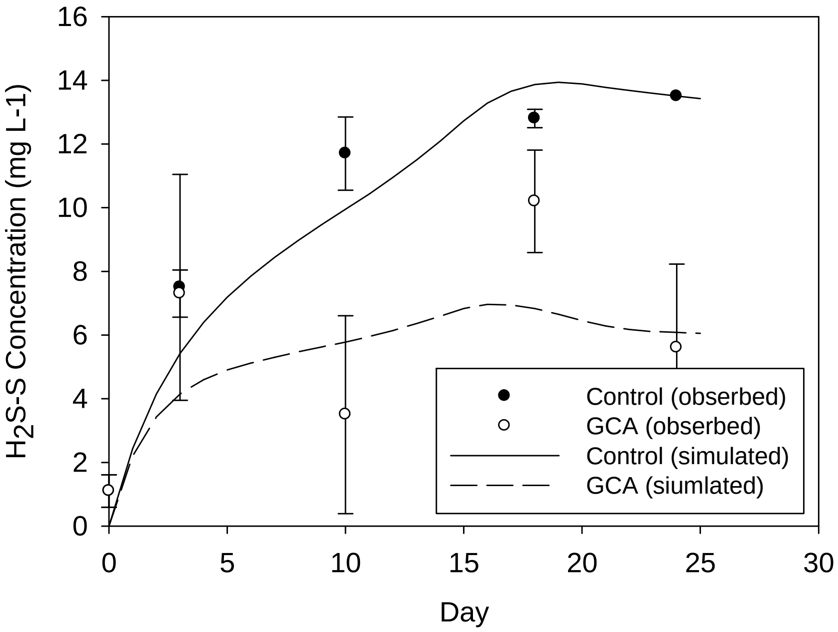


Fig. 4 Simulated and observed hydrogen sulfide concentration in sediment pore water at Ohko Inlet

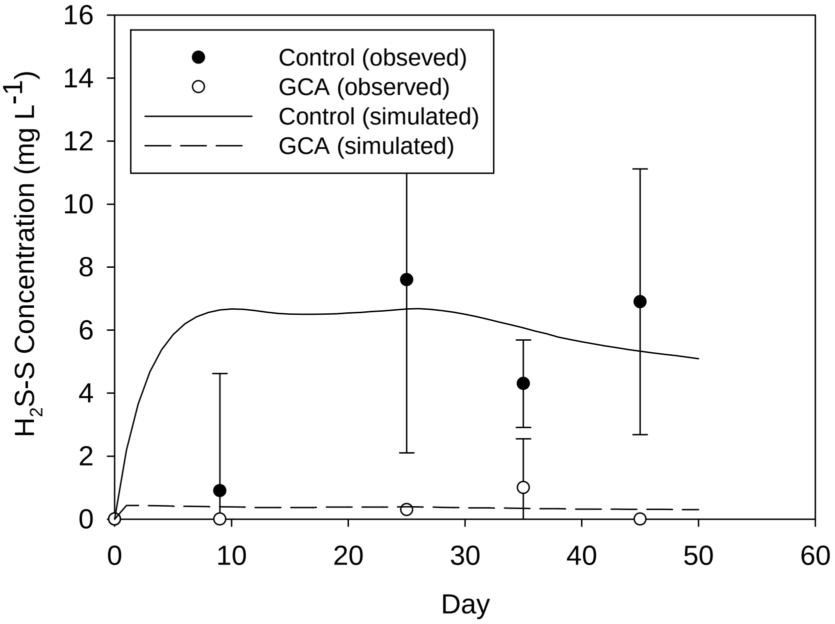


Fig. 5 Simulated and observed hydrogen sulfide concentration in sediment pore water at Ohzu Inlet

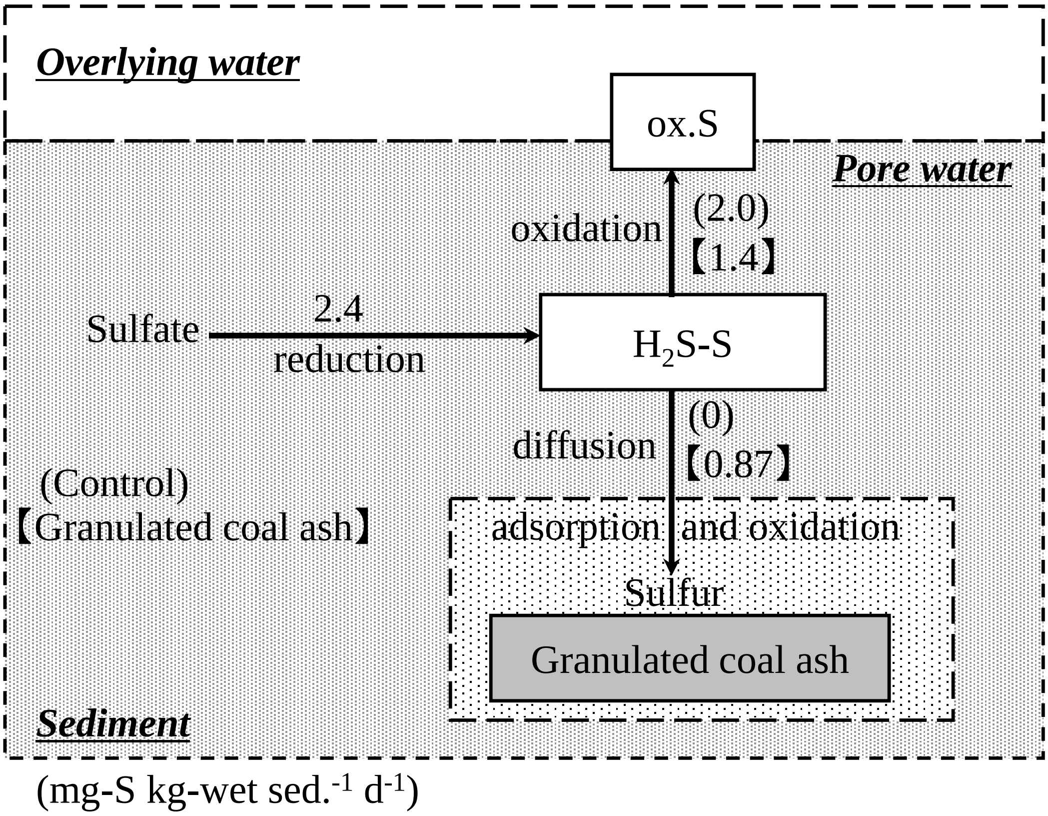
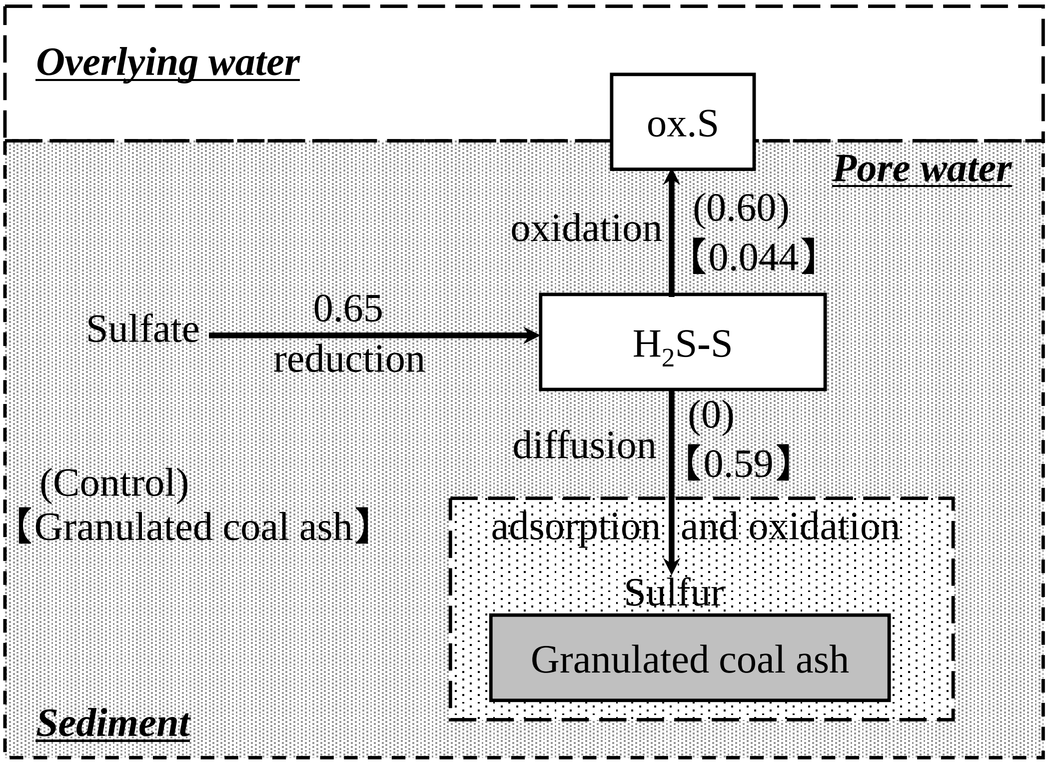


Fig. 6 Calculated daily average of sulfur flow in Ohko Inlet sediment



(mg-S kg-wet sed.$^{-1}$ d^{-1})

Fig. 7 Calculated daily average of sulfur flow in Ohzu Inlet sediment

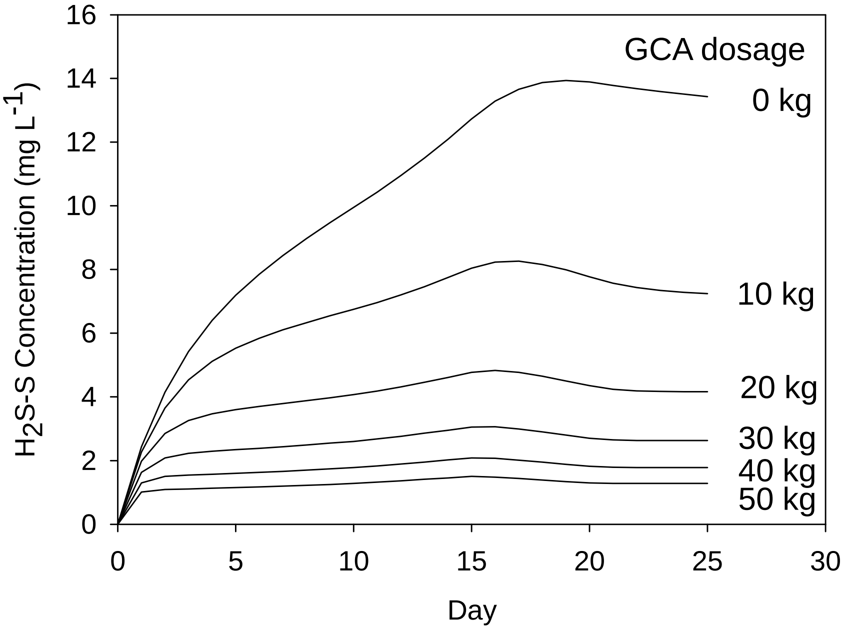


Fig. 8 Calculated concentration of hydrogen sulfide in sediment pore water with various the granulated coal ash application dosage at Ohko Inlet

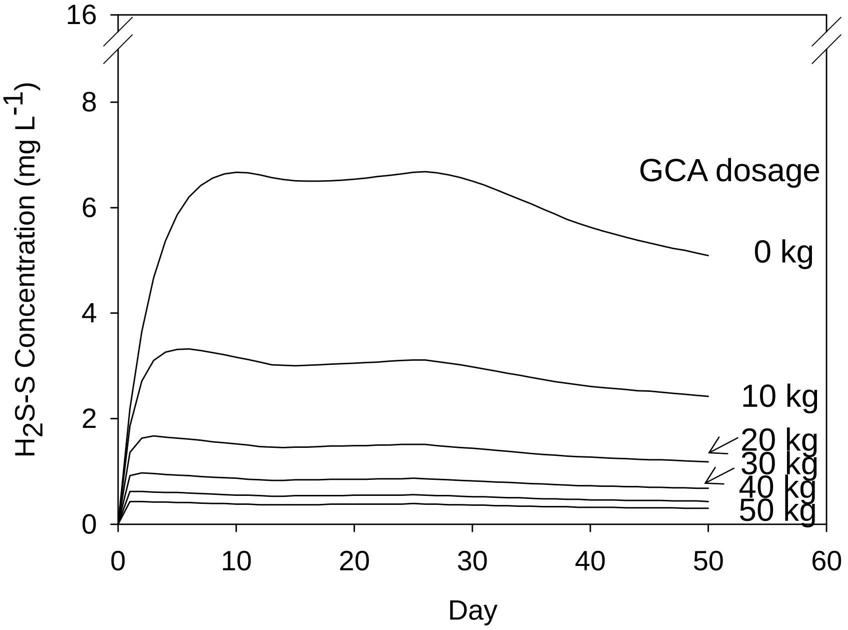


Fig. 9 Calculated concentration of hydrogen sulfide in sediment pore water with various the granulated coal ash application dosage at Ohzu Inlet

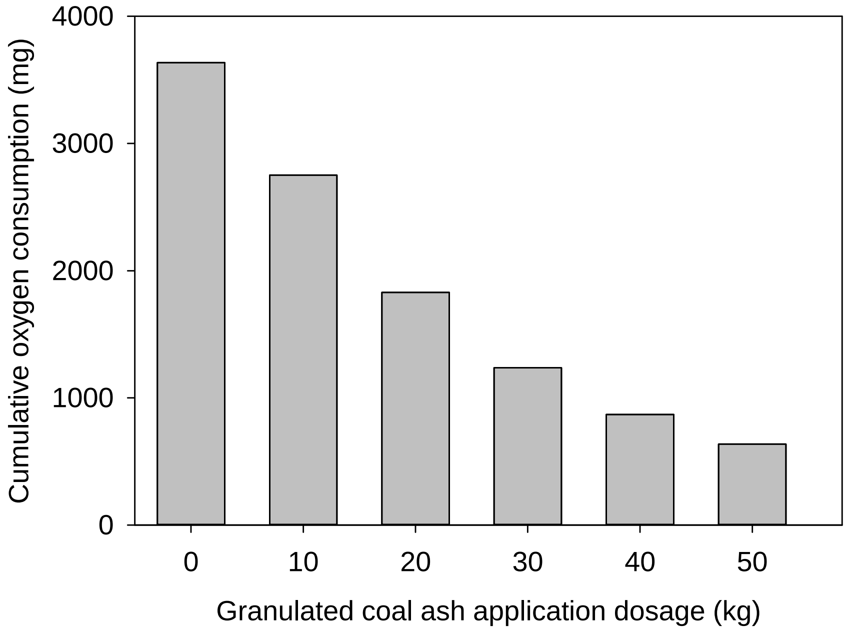


Fig. 10 Cumulative oxygen consumption of Ohko Inlet throughout the experimental periods

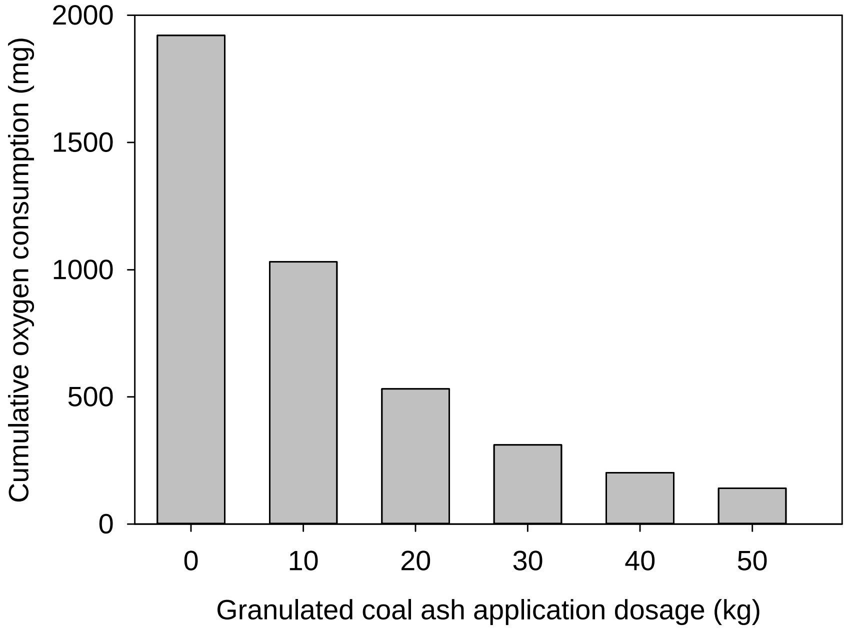


Fig. 11 Cumulative oxygen consumption of Ohzu Inlet throughout the experimental periods

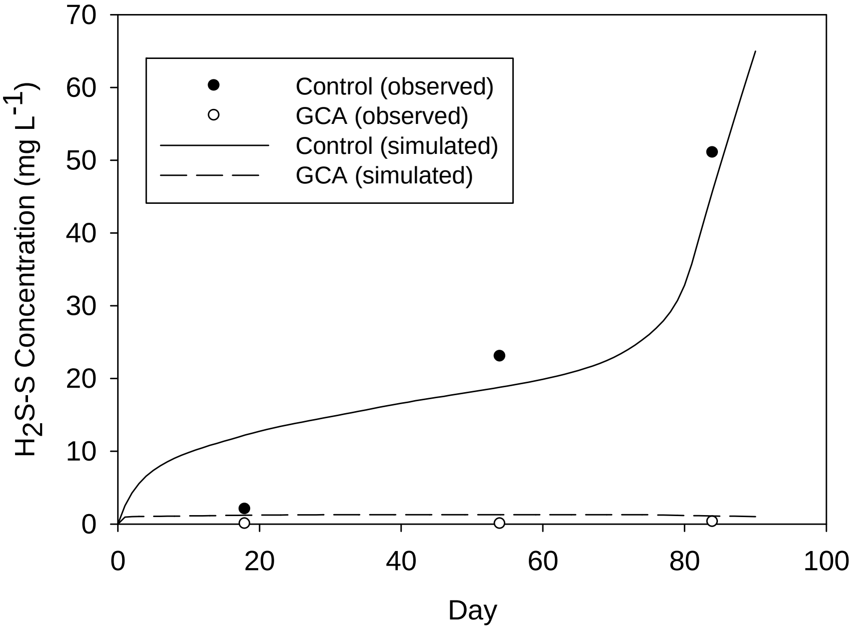


Fig. 12 Simulated and observed hydrogen sulfide concentration in sediment pore water of the field experiment

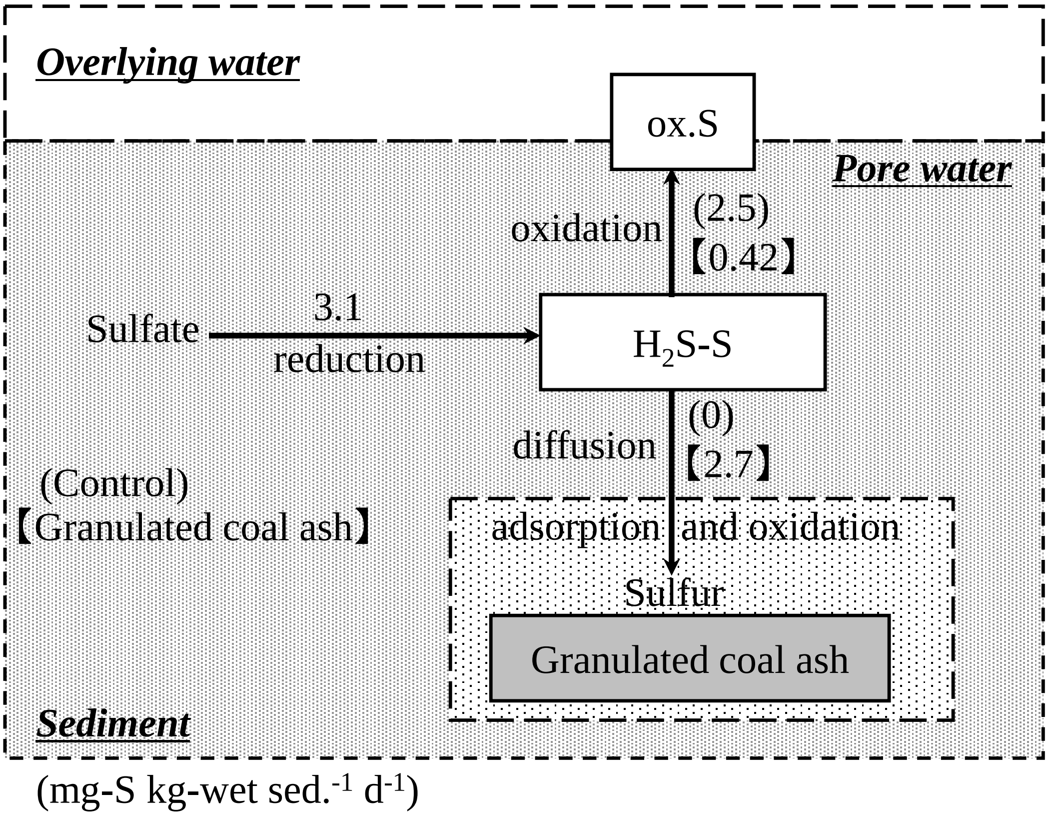


Fig. 13 Calculated daily sulfur flow of the field experiment

Table

Table 1 Parameters used in the proposed model

Definition	Value	Unit	References
cell density of sulfate reducing bacteria in marine sediment (Ohko Inlet)	60000	cells g^{-1} dry weight	Asaoka et al., 2009d
cell density of sulfate reducing bacteria in marine sediment (Ohzu Inlet)	10000	cells g^{-1} dry weight	Asaoka et al., 2009d
cell density of sulfate reducing bacteria in marine sediment (Field experiment)	44700	cells g^{-1} dry weight	Asaoka et al., 2009d
molecular diffusion coefficient	6.00×10^{-5}	$m^2\ d^{-1}$	Li et al. 1974
removal rate of hydrogen sulfide	1.03	d^{-1}	Asaoka et al., 2009b
reduction rate of sulfate by sulfate reducing bacteria at 30 °C	7.7×10^{-7}	mg L^{-1} $cell^{-1}$ d^{-1}	Canfield et al., 2006
retardation coefficient	1.0×10^{6}	-	Parameter fitting
specific surface area of the granulated coal ash	21.1	$m^2\ g^{-1}$	Asaoka et al., 2008