

## Suppression of nutrient release from freshwater lake sediments using granulated coal ash

Takehiko Fukushima, Masako Okabe, Tadashi Hibino, Narong Touch and Kenji Nakamoto

### ABSTRACT

In order to investigate the applicability of granulated coal ash (GCA), a by-product of coal thermal power stations, to freshwater lakes, two incubation experiments (fall and summer experiments) were conducted using large-volume vessels and sediments taken from eutrophic lakes. The phosphorus and nitrogen release fluxes in the vessels with GCA (up to  $2.9 \text{ mg m}^{-2} \text{ d}^{-1}$  for total phosphorus and  $23.9 \text{ mg m}^{-2} \text{ d}^{-1}$  for total nitrogen) were considerably smaller than those in the vessels without GCA (up to  $8.9 \text{ mg m}^{-2} \text{ d}^{-1}$  and  $56 \text{ mg m}^{-2} \text{ d}^{-1}$ , respectively), except in the case of phosphorus in the fall experiment, and thus the phosphorus concentration released from the vessel without GCA under anoxic conditions in the summer experiment was extraordinarily higher (over  $1.5 \text{ mg l}^{-1}$ ) than those in the other vessels (less than  $0.31 \text{ mg l}^{-1}$ ). Supplementary experiments with smaller columns indicated that the chemical effect of GCA was on a similar level with its physical effect and that the threshold phosphorus concentration for removing it was lower in freshwater than seawater. The chromium level slightly exceeded the standard for drinking water and the development of technology to suppress its release is a future challenge.

**Key words** | eutrophic lake, granulated coal ash, nutrient release, sediments, toxic chemicals

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### INTRODUCTION

Eutrophication, which is caused by the response of natural waters to excessive inputs of nutrients, is one of the biggest environmental problems facing humanity (Schindler *et al.* 2016). Cyanobacterial blooms resulting from eutrophication are becoming more frequent, more intense, and more widespread in aquatic environments and have many adverse effects on ecosystems and human health (O'Neil *et al.* 2012; Bormans *et al.* 2016). In order to restore lake environments, it is crucial to reduce their nutrient loads via point and nonpoint sources in an effective manner.

Nutrient dynamics in shallow lakes are different from those in deep dimictic lakes and sediment–water exchanges

play a much greater role because they quickly and largely affect biological activities in upper waters (Havens *et al.* 2001). Thus, a strong emphasis is placed on the reduction or control of the internal nutrient load from sediments by means including physical, chemical, and biological methods (Bormans *et al.* 2016). Chemical approaches mainly aim to reduce the phosphorus (P) release from sediments by improving the P-binding capacity. Some of the materials investigated included iron oxides, red mud, fly ash, and carbonates; recently, alum, calcite, Phoslock™ and modified zeolite have been applied to actual bodies of water (Zamparas & Zacharias 2014). Sediment capping with

sand is one physical method used to rehabilitate contaminated sediments (Galvez-Cloutier *et al.* 2006).

Granulated coal ash (GCA) is a by-product of coal thermal power stations. A laboratory experiment with a flow-through system indicated that GCA remediated coastal marine sediments by reducing benthic P flux and hydrogen sulfide (Asaoka *et al.* 2009). The kinetics by which P from seawater is remediated by GCA under both oxic and anoxic conditions were investigated using batch experiments, and it was found that GCA could remove phosphate from seawater effectively under anoxic conditions (Asaoka & Yamamoto 2010). Batch laboratory experiments revealed that hydrogen sulfide was adsorbed on GCA and successively oxidized by manganese oxide (III) contained in the GCA (Asaoka *et al.* 2012, 2014). Field experiments for remediation of coastal sediments successfully demonstrated the usefulness of GCA in estuarine rivers and coastal areas (Yamamoto *et al.* 2013, 2015; Kim *et al.* 2014). In a brackish water lake, field experiments showed that capping with GCA reduced the release fluxes of nutrients and hydrogen sulfide from sediments (Kido *et al.* 2014) and remediated the living conditions of bivalves (Fukuma *et al.* 2009).

In contrast to seawater and brackish water areas, the applicability of GCA to freshwater lakes has not been examined due to uncertainty regarding its effectiveness in nutrient suppression and the risk of releasing toxic chemicals. In the present paper, experiments were conducted to measure the ability of GCA to suppress nutrient release from lake sediments and to investigate the mechanism of the suppression in freshwater environments while monitoring the release of toxic chemicals from GCA. The study incorporates: (1) long-term experiments that take seasonal change into account, i.e. two experiments around a half-year long mainly focused on fall and summer, respectively, to evaluate the suppression ability of GCA by emulating the field conditions; (2) these long-term experiments with large-volume vessels under seven different conditions; and (3) five kinds of supplementary experiments with smaller columns or bottles (No. 1: four columns, No. 2: three columns, No. 3: four columns, No. 4: four columns, and No. 5: 24 bottles) that support understanding the factors affecting the suppression ability of GCA. Large-volume vessels were used to reduce the inhomogeneity that results from

the rather large size of GCA particles and to minimize the influences of water sampling and/or side-wall on the long-term experiments. Although replication of the experiments was required due to the scatter of the results, unreplicated experiments were done according to a large number of experimental conditions to be investigated for roughly figuring out the suppression ability of GCA.

## MATERIALS AND METHODS

### Materials

The GCA used in this study was provided by Chugoku Electric Power Co., Inc., Hiroshima, Japan. Fly ash produced at the Shin-Onoda coal power plant was pulverized and granulated to coarse grains with a 2 cm diameter on average using cement (weight mixing ratio: 15%) as a binder. No further additive was added. The GCA was mainly composed of SiO<sub>2</sub>, AlO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, and CaO/MgO comprising quartz and aluminosilicate crystals at concentrations of 510, 205, 70 and 100 g kg<sup>-1</sup>, respectively. Its specific density was about 2.4.

A few days before the start of the experiments, surface sediments up to 20 cm in depth were sampled from the centers of Lake Kasumigaura (the fall experiments explained below) and Lake Kitaura (the summer experiments) using a Smith-McIntyre grab sediment sampler and then mixed well. The compositions of sediments are shown in Table 1. Water that had undergone sand filtration in the Ami water purification plant, which uses water from Lake Kasumigaura, was used to fill the experimental vessels. This water was stored near the vessels during the experimental periods and used to compensate the loss caused by water sampling as explained below. Both Lake Kasumigaura (which has a surface area of 172 km<sup>2</sup> and a mean depth of 4.0 m) and Lake Kitaura (with a surface area of 36 km<sup>2</sup> and a mean

**Table 1** | Compositions of sediments for incubation experiments

	P	N	C
	mg g (dry) <sup>-1</sup>		
Fall experiment	1.0	7.2	58.6
Summer experiment	1.0	9.1	65.1

depth of 4.8 m) are shallow, eutrophic lakes where the nutrient release from the sediments is suspected to be the main cause of persistent eutrophication in spite of the intense management of the loads from the basins (Kamiya *et al.* 2017). For example, the riverine TP (total phosphorus) concentrations decreased from  $0.36 \text{ mg l}^{-1}$  in 1981 to  $0.10 \text{ mg l}^{-1}$  in 2014 in Lake Kasumigaura and from  $0.29 \text{ mg l}^{-1}$  in 1985 to  $0.089 \text{ mg l}^{-1}$  in 2014 in Lake Kitaura, respectively. The average concentrations of TP and TN (total nitrogen) in these lakes were around  $0.1 \text{ mg l}^{-1}$  and  $1 \text{ mg l}^{-1}$ , respectively (from 2001 to 2010: Fukushima & Arai 2015), showing indistinct long-term changes. In addition, Lakes Kasumigaura and Kitaura are polymictic lakes and anoxic conditions are expected near the sediments when an event of strong blowing wind does not arise over several days (Kamiya *et al.* 2017).

### Experiment settings (main experiment)

Seven vessels with a diameter of 435 mm and a height of 880 mm were used for the incubation experiments. In the fall experiment, four settings in oxic vessels (F1: no GCA, F2: 5 cm GCA, F3: 15 cm GCA, F4: 15 cm GCA with no sediments) and three settings in anoxic vessels (F5: no GCA, F6: 5 cm GCA, F7: 15 cm GCA) were designed to investigate the effects of GCA on the water columns as shown in Figure 1. In the summer experiments, three settings in oxic vessels (S1: no GCA, S2: 10 cm GCA, S3: 10 cm GCA with resuspended sediments) and four settings in anoxic vessels (S4: no GCA, S5: 10 cm GCA, S6: 10 cm GCA with resuspended sediments, S7: 5 cm GCA) were also made (Figure 1). The settled sediments (S3 and S6) simulated the deposition of resuspended sediments (RS) on the GCA layers. This kind of deposition is expected to occur in large shallow lakes, e.g., Lake Kasumigaura (Fukushima & Arai 2015). Crushed rocks wrapped in plastic bags were used for adjusting the water depth. Oxic vessels were stirred continuously by air-pump. Anoxic vessels were covered by doubled vinyl sheets (fall experiment) or plastic lids (summer experiment) to minimize the intrusion of air, and the water in them was gently but continuously mixed by magnetic stirrers to make the water uniform. The water samples (250 ml for sensor analyses, 125 ml for no-filtration, and 250 ml for filtration) in oxic and anoxic vessels

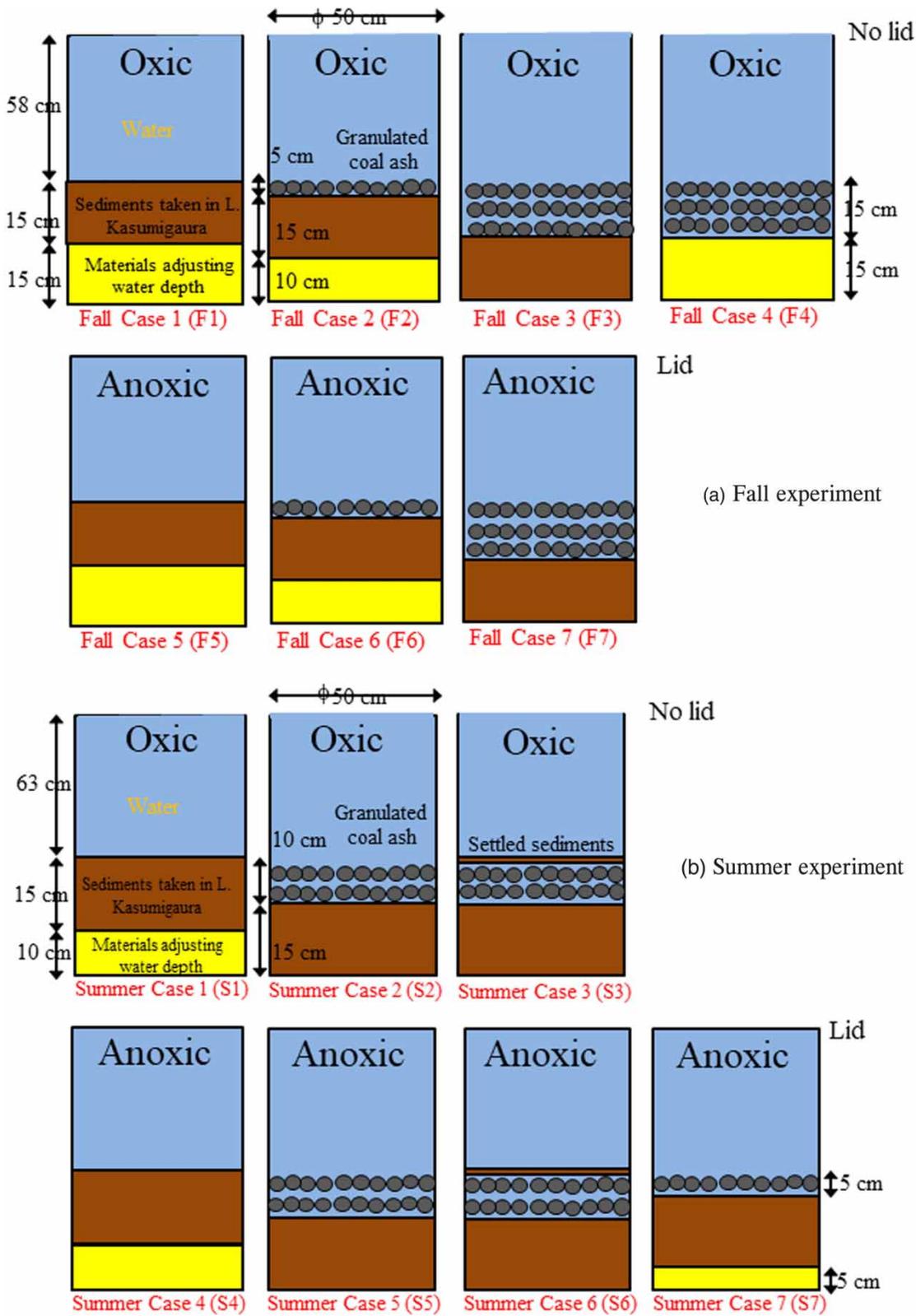
were taken using a siphon system at the middle depth of the water column while it was assumed that the waters probably had no vertical profiles of water quality. These vessels were set in a dark tank where water with a depth of around 60 cm was stored. In this tank, the water temperature changed according to the outdoor air temperature.

### Water sampling and analysis

The fall and summer experiments were conducted from August 26, 2014 to February 17, 2015 (174 days), and from May 16, 2015, to November 17, 2015 (185 days), respectively. The measured items are summarized in Table 2. Whatman GF/F filters were used for filtration of the water samples.

A D-54 potable water quality meter (Horiba Ltd, Kyoto, Japan) was used to measure the water temperature (WT), pH, electrical conductivity (EC), and oxidation/reduction potential (ORP) in sampled waters. A professional ODO Water Quality Instrument (YSI Inc., Ohio, USA) was also used for the measurement of dissolved oxygen (DO) concentrations.

Nutrient concentrations, i.e., TP, dissolved TP (DTP), soluble reactive P ( $\text{PO}_4\text{-P}$ ), TN, dissolved TN (DTN), nitrate-N ( $\text{NO}_3\text{-N}$ ), nitrite-N ( $\text{NO}_2\text{-N}$ ), and ammonium-N ( $\text{NH}_4\text{-N}$ ), were analyzed using continuous flow analyzers (Auto Analyzer 3 and AACS-III, BRAN + LUEBBE, Norderstedt, Germany) after digestion with potassium peroxodisulfate in the case of the measurements of TP, DTP, TN and DTN. Concentrations of major ions, i.e., sodium ( $\text{Na}^+$ ), potassium ( $\text{K}^+$ ), magnesium ( $\text{Mg}^{2+}$ ), calcium ( $\text{Ca}^{2+}$ ), chloride ( $\text{Cl}^-$ ), and sulfate ( $\text{SO}_4^{2-}$ ), were analyzed with an ion chromatograph analyzer (ICS-2000, DIONEX Co., CA, USA). The alkalinity of the water was determined by titration using sulfuric acid. The concentrations of dissolved silicon (DSi) were determined by the colorimetric method (UV-2450, Shimadzu Co., Kyoto, Japan) and those of iron (Fe) and manganese (Mn) were analyzed with inductively coupled plasma spectrometry (ICPS-8100, Shimadzu). The concentrations of total organic carbon (TOC) were determined using a TOC analyzer (TOC-V CSH, Shimadzu). The pretreatment for measuring heavy metal concentrations was as follows: (1) the addition of 0.5 ml nitrate into a 10 ml sample, (2) heat-concentration to around 5 ml, (3) dilution in a measuring cylinder to 10 ml total, and (4) filtration with a membrane



**Figure 1** | Experimental settings of seven vessels: (a) fall experiment, (b) summer experiment.

**Table 2** | Measurement, sampling, and analysis of water and sediment samples in the incubation experiments

	Period	Type	Items	Days after the start
Fall experiment (F1 – F7)	Aug. 26, 2014–Feb. 17, 2015 (174 days)	Water measurement	WT, pH, EC, ORP, DO	0, 2, 4, 6, 8, 10, 15, 23, 31, 44,
		Water sampling and analysis	Nutrients, major ions, alkalinity, Fe, Mn, Si, toxic chemicals	60, 77, 105, 122, 135, 154, 164, 174
		Sediment sampling and analysis	Water content, carbon, nitrogen and phosphorus content	0, 174
Summer experiment (S1 – S7)	May, 16, 2015– Nov. 17, 2015 (185 days)	Water measurement	WT, pH, EC, ORP, DO	0, 2, 4, 6, 8, 10, 14, 31, 45, 60,
		Water sampling and analysis	Nutrients, major ions, alkalinity, Fe, Mn, Si, TOC, toxic chemicals	75, 83, 103, 122, 136, 151, 164, 185
		Sediment sampling and analysis	Water content, carbon, nitrogen and phosphorus content	0, 185

WT: water temperature, EC: electric conductivity, DO: dissolved oxygen, ORP: oxidation/reduction potential.

Nutrients: TP (total phosphorus), dissolved total phosphorus (DTP), soluble reactive phosphorus (PO<sub>4</sub>-P), total nitrogen (TN), total dissolved nitrogen (DTN), nitrate–nitrogen (NO<sub>3</sub>-N), nitrite–nitrogen (NO<sub>2</sub>-N), and ammonium–nitrogen (NH<sub>4</sub>-N).

Major ions: sodium (Na<sup>+</sup>), potassium (K<sup>+</sup>), magnesium (Mg<sup>2+</sup>), calcium (Ca<sup>2+</sup>), chloride (Cl<sup>-</sup>), sulfate (SO<sub>4</sub><sup>2-</sup>).

Toxic chemicals: chromium (Cr), copper (Cu), arsenic (As), selenium (Se), cadmium (Cd) and lead (Pb).

Analysis was not done on all days (see Figures 2 and 3, and Supplementary Figures (a)–(h), available with the online version of this paper).

filter (0.2 μm pore size, ADVANTEC). Then, the concentrations of arsenic (As), cadmium (Cd), chromium (Cr), copper (Cu), lead (Pb), and selenium (Se) were determined as toxic chemicals with plasma mass spectrometry (Elan Drc-e, Perkin Elmer Co., MA, USA).

The C and N contents of the dried samples were analyzed with a CHNS analyzer (CHNS/0 2400 II, Perkin Elmer Co.), and their P contents were determined by a method similar to the water analysis.

## Supplementary experiments

### Supplementary experiment (1): experiment concerning different water depths

To investigate the influence of water depth on the rates of nutrient release under anoxic conditions, four plastic columns with an inner diameter of 10 cm and a length of 50 cm were set up in a dark tank as follows: (A) 36 cm water + 9 cm sediments (summer experiments) + 5 cm depth-adjusting sand, (B) 36 cm water + 5 cm GCA + 9 cm sediments, (C) 18 cm water + 9 cm sediments + 23 cm depth-adjusting sand, and (D) 18 cm water + 5 cm GCA + 9 cm sediments + 18 cm depth-adjusting sand. The water after sand filtration was used. Both sides of the columns were covered by rubber caps. At 7 days after the

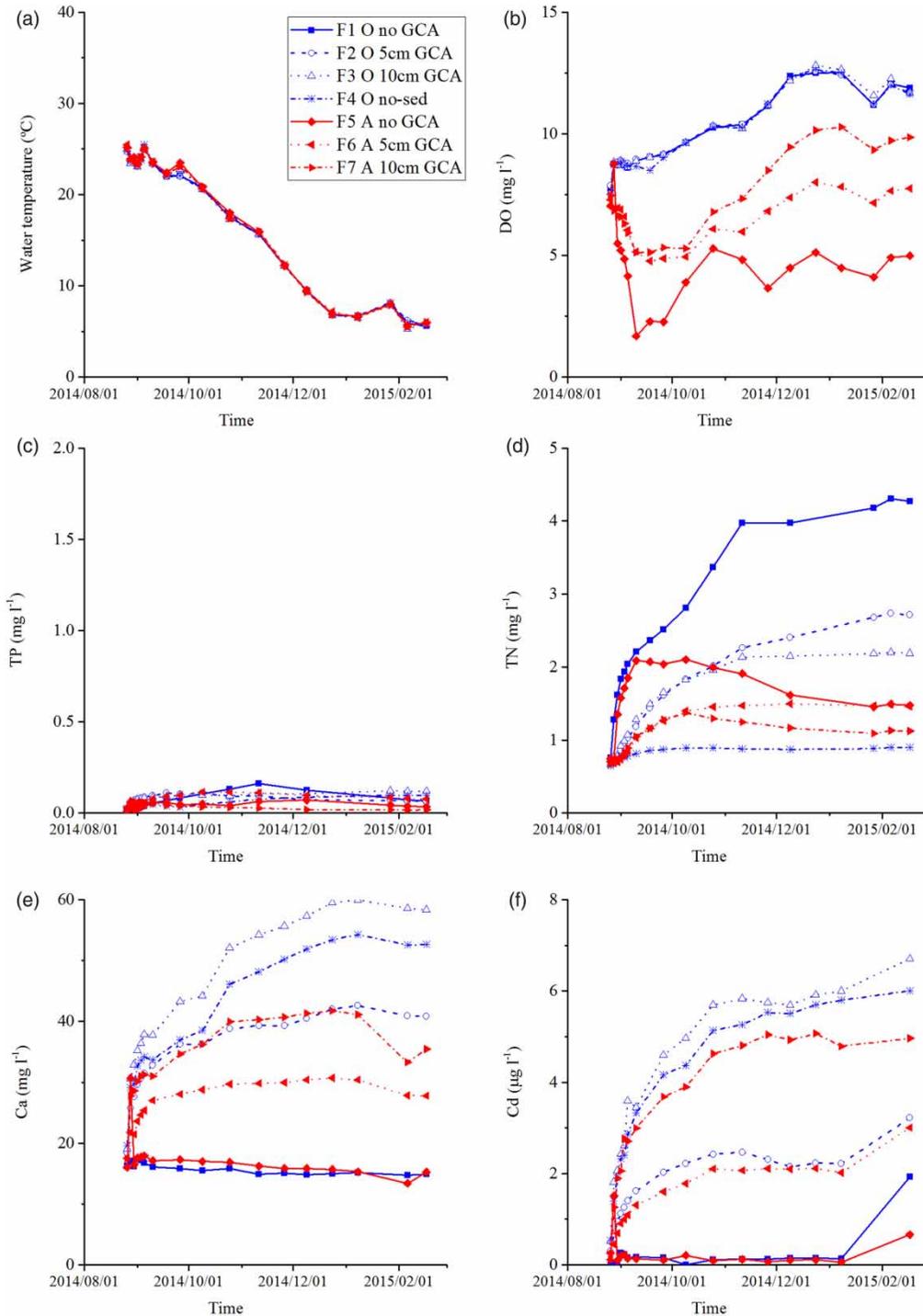
start of the experiment, water samples were taken for the measurement of nutrients.

### Supplementary experiment (2): experiment comparing physical and chemical effects

To compare the mechanisms of the suppression of nutrient release between physical and chemical processes under anoxic conditions, three plastic columns similar to those used in supplementary experiment (1) were set up in the dark tank as follows: (E) 36 cm water + 9 cm sediments + 5 cm depth-adjusting sand, (F) 36 cm water + 5 cm GCA + 9 cm sediments and (G) the same setting as (E), but with GCA (amount equal to 5 cm GCA in (F)) hung in a mesh bag near the center of the water. At 30 days after the start of the experiment, water samples were taken for the measurement of nutrients.

### Supplementary experiment (3): experiment comparing freshwater and seawater

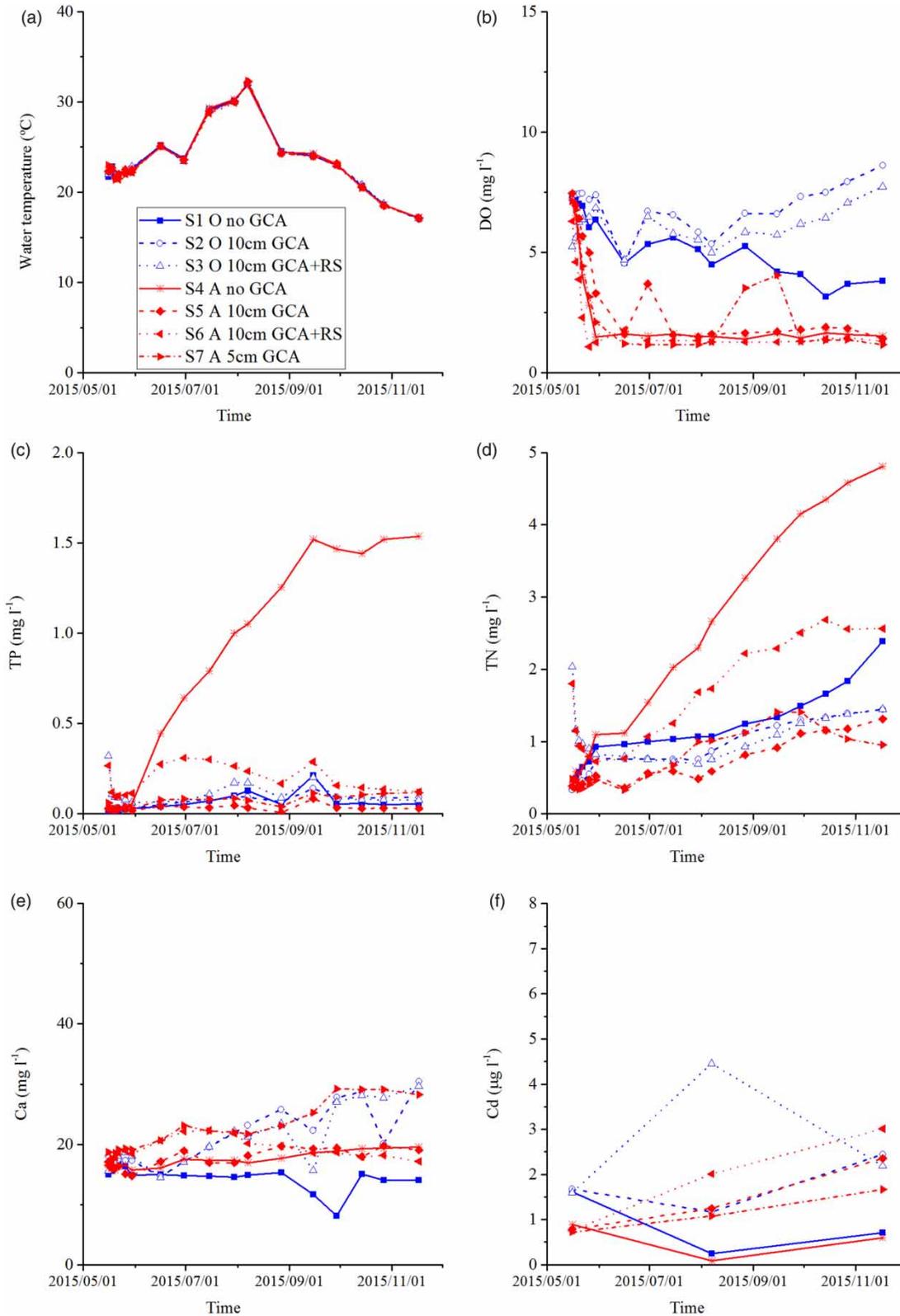
To compare the ability to suppress nutrients between freshwater and seawater under anoxic conditions, four plastic columns with an inner diameter of 7 cm and a length of 44.5 cm were set as follows: (H) 32 cm water (freshwater same as supplementary experiment (1)) + 7.5 cm sediments + 5 cm depth adjusting sand, (I) 32 cm seawater (artificial



**Figure 2** | Temporal changes of the representative water-quality parameters in the vessels during the fall experiment: (a) water temperature, (b) DO, (c) TP, (d) TN, (e) Ca, (f) Cd.

seawater: Yashimachem. Co., Ltd, Osaka, Japan) + 7.5 cm sediments + 5 cm depth adjusting sand, (J) 32 cm water (freshwater) + 5 cm GCA + 7.5 cm sediments, and (K)

32 cm seawater + 5 cm GCA + 7.5 cm sediments. They were left in a dark constant-temperature room at 25°C, subsamples were taken at 11, 21, 30 and 95 days after the start



**Figure 3** | Temporal changes of the representative water-quality parameters in the vessels during the summer experiment: (a) water temperature, (b) DO, (c) TP, (d) TN, (e) Ca, (f) Cd.

of this experiment, and the nutrient concentrations were determined. The DO concentration was monitored using the DO meter as described previously.

#### Supplementary experiment (4): experiments comparing GCA and sand

To compare the ability to suppress nutrients between GCA and sand (with a diameter of a few hundred micrometres), four plastic columns with an inner diameter 7 cm and a length of 44.5 cm were set as follows: (L) 32 cm water (same as supplementary experiment (4)) + 5 cm GCA + 7.5 cm sediments under oxic conditions, (M) 32 cm water + 5 cm sand + 7.5 cm sediments under oxic conditions, (N) 32 cm water + 5 cm GCA + 7.5 cm sediments under anoxic conditions, and (O) 32 cm water + 5 cm sand + 7.5 cm sediments under anoxic conditions. The water sampling was the same as in supplementary experiment (3).

#### Supplementary experiment (5): experiment determining the relationship between equilibrium phosphate concentration and adsorbed P on GCA

About 1 g of GCA was put into each of 24 plastic bottles with a volume of 50 ml. Then, four cases were set up with six bottles each as follows to check the influence of the surface-to-volume ratio of GCA on the equilibrium: (i) 0.5 cm diameter GCA in freshwater, (ii) 1 cm diameter GCA in freshwater, (iii) 0.5 cm diameter GCA in seawater, and (iv) 1 cm diameter GCA in seawater. Forty-five-millilitre volumes of water with six  $\text{PO}_4\text{-P}$  concentrations (0, 0.031, 0.062, 0.155, 0.775 and  $1.55 \text{ mg l}^{-1}$ ) were respectively put into the six bottles, and they were shaken continuously. Asaoka & Yamamoto (2010) reported that 14 days of stirring were sufficient to reach the equilibrium state between GCA and  $\text{PO}_4\text{-P}$  for seawater experiments. To be cautious,  $\text{PO}_4\text{-P}$  concentrations of the water in the bottles were analyzed at 28 days after the start of the experiment, and the adsorption isotherm (equilibrium  $\text{PO}_4\text{-P}$  concentration vs net adsorbed onto GCA) was determined for each case. The net amount adsorbed corresponds to the adsorbed minus the desorbed amount calculated based on the change in the  $\text{PO}_4\text{-P}$  concentration in the water phase.

Less reliability in the results of the supplementary experiments was expected compared with those of the main experiments because the scatter due to the impact of GCA size on the experiments was larger in the supplementary experiments.

## RESULTS

### Water-quality changes in main experiments

The changes in representative water-quality parameters during the fall and summer experiments are shown in Figures 2 and 3, respectively, and those of other parameters are indicated in Supplementary Figures (a)–(h) (available with the online version of this paper). The ratios of the maximum concentrations during the experimental period to the initial concentrations of the respective items are summarized in Table 3. In general, the nutrient concentrations showed larger ratios, particularly in the summer experiment. Major ions yielded values close to unity, indicating that the changes were not very drastic. In the case of toxic chemicals, the ratios were higher in the fall experiment compared with the summer experiment, possibly resulting from the smaller sample numbers in the latter.

In the fall experiment, the water temperature was gradually decreased. The DO concentrations in anoxic vessels showed minimums in September and then increased (similar to ORP). The TP concentrations (similar to DTP and  $\text{PO}_4\text{-P}$ ) rapidly increased during the first 15 days and did not show a clear change after this period whether they were in oxic or anoxic tanks. The TN concentrations (similar to  $\text{NO}_3\text{-N}$ ) showed gradual increases and the vessels without GCA (referred to as 'no-GCA vessels') showed higher increases compared with the vessels with GCA (referred to as 'GCA vessels'). Both of the  $\text{Ca}^{2+}$  and Cd concentrations increased in the GCA vessels while unclear increases were observed in the no-GCA vessels (similar to pH,  $\text{K}^+$ ,  $\text{SO}_4^{2-}$ , and As); in contrast, the  $\text{Mg}^{2+}$  concentration decreased in the GCA vessels.

In the summer experiment, water temperature reached its maximum in August. The DO concentrations in the anoxic vessels showed rapid decreases during the first 15 days, and thereafter maintained nearly constant values around  $2 \text{ mg l}^{-1}$ . The TP concentration in S4 (anoxic

**Table 3** | Ratio of maximum concentration during the incubation experiment to initial concentration

	TP	DTP	P <sup>*1</sup>	TN	DTN	N1 <sup>*2</sup>	N2 <sup>*3</sup>	N3 <sup>*4</sup>	EC	A <sup>*5</sup>	Na	K	Mg	Ca	Cl	SO <sub>4</sub>	Fe	DSi	TOC	Cr	Cu	As	Se	Cd	
<b>(1) Fall experiment</b>																									
F1 O no GCA	15.0	11.4	13.0	5.7	5.6	7.4	121	5.8	1.5	1.1	1.5	1.1	1.1	1.1	1.4	2.0	4.0	11.7						2.3	
F2 O 5 cm GCA	5.6	8.9	9.2	4.1	4.2	5.0	24.5	3.0	1.7	1.1	1.4	1.8	1.0	2.3	1.3	2.5	2.2	3.0		31.4	12.4	146	1.8	10.9	
F3 O 15 cm GCA	5.4	7.5	8.8	3.3	3.4	4.0	16.3	2.6	2.0	1.1	1.4	2.3	1.0	3.1	1.3	3.7	3.1	1.6		35.6	6.4	16.2	2.8	12.9	
F4 O no-sed	4.4	5.8	6.6	1.4	1.4	1.6	1.5	2.7	1.7	1.0	1.2	2.2	1.0	2.8	1.1	3.5	2.6	1.7		26.8	3.2	14.4	2.6	11.3	
F5 A no GCA	7.6	15.2	13.2	2.8	2.8	3.5	36.0	16.8	1.3	1.2	1.2	2.6	1.2	1.9	1.2	1.9	2.7	13.7		43.1	1.0		1.6	5.9	
F6 A 5 cm GCA	3.8	9.8	11.3	2.1	2.4	2.6	11.5	3.7	1.4	1.1	1.1	1.9	1.0	1.7	1.1	1.9	3.6	2.9		117	17.0		2.2	26.6	
F7 A 15 cm GCA	3.6	5.1	6.6	2.1	2.1	2.0	13.0	4.4	1.6	1.0	1.2	2.6	1.0	2.4	1.1	3.0	12.5	4.4		370	14.1		3.7	49.2	
<b>(2) Summer experiment</b>																									
S1 O no GCA	19.1	194	79.1	6.9	7.7	12.9	21.7	21.9	1.4	1.2	1.5	3.1	1.1	1.1	1.4	3.1	1.0	26.2	1.9	1.1	10.6	3.0	1.0	1.0	
S2 O 10 cm GCA	5.8	19.6	7.5	4.4	5.2	11.0	19.1	1.8	1.3	1.0	1.3	2.1	1.0	1.7	1.4	2.1	1.4	8.4	1.6	2.7	1.1	11.1	1.4	1.5	
S3 O 10 cm GCA + SS	1.0	48.0	21.4	1.0	2.1	10.1	13.0	1.0	1.4	1.3	1.4	1.6	1.0	1.9	1.4	1.6	1.2	10.1	2.0	1.2	2.4	4.6	1.6	2.8	
S4 A no GCA	107	1,510	1,420	12.7	17.6	1.2	34.0	84.4	1.3	2.0	1.2	1.2	1.2	1.2	1.1	1.2	13.0	23.3	1.8	1.8	2.9	2.2	2.0	1.0	
S5 A 10 cm GCA	3.1	62.5	5.3	3.5	4.6	3.1	17.8	24.3	1.2	1.0	1.2	2.1	1.0	1.2	1.1	2.1	1.2	6.8	1.5	1.1	4.4	11.9	2.1	3.0	
S6 A 10 cm GCA + SS	1.2	114	44.2	1.5	4.4	1.9	12.4	7.7	1.1	1.1	1.1	1.9	1.0	1.4	1.1	1.9	1.1	9.5	2.5	1.0	5.0	11.7	1.8	4.0	
S7 A 5 cm GCA	2.0	23.1	10.7	2.9	5.3	9.8	36.0	24.4	1.2	1.0	1.1	1.8	1.0	1.6	1.1	1.8	1.6	5.5	1.6	1.6	2.4	11.5	1.6	2.3	

\*1: PO<sub>4</sub>-P, \*2: NO<sub>3</sub>-N, \*3: NO<sub>2</sub>-N, \*4: NH<sub>4</sub>-N, \*5: alkalinity.  
 O: oxic, A: anoxic. F1 – F7 and S1 – S7: see Figure 1.

without GCA) increased at a much faster rate compared with those in the other vessels, and its maximum (around  $1.5 \text{ mg l}^{-1}$ ) was particularly higher than the other vessels in both of the experiments (less than  $0.31 \text{ mg l}^{-1}$ ) (similar to Fe, Mn). The changes in TP were due to those in  $\text{PO}_4\text{-P}$ . The TN concentrations showed gradual increases, and especially high increase rates were observed in S1 (oxic without GCA), S4, and S6 (anoxic with GCA and SS) (similar to TOC). Unlike in the fall experiment, these increases were attributed to those of  $\text{NH}_4\text{-N}$ . The change patterns in  $\text{Ca}^{2+}$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{SO}_4^{2-}$ , Cd, As and pH were the same as those in the fall experiment. Si concentrations showed gradual increases, particularly in no-GCA vessels, in both the fall and summer experiments.

#### GCA behavior in supplementary experiments (1)–(4)

At first, the differences between the concentrations after the experiments and the initial concentration were calculated in the respective cases and then these differences were compared as the ratios. In supplementary experiment (1), these ratios of the nutrient concentration increases from the initial state ((C)/(A): 1.70 for  $\text{PO}_4\text{-P}$  and 1.59 for  $\text{NH}_4\text{-N}$  and (D)/(B): 1.26 for  $\text{PO}_4\text{-P}$  and 2.61 for  $\text{NH}_4\text{-N}$ ; Figure 4(a)–4(b)) were in roughly reverse proportion to the water depth (36 cm vs 18 cm). In the case of TP, the ratios (C)/(A) and (D)/(B) were 1.37 and 1.41, respectively, and in the case of TN, they were 1.94 and 1.57, respectively. In supplementary experiment (2), the use of bottom GCA greatly reduced the ratios of nutrient concentration increase from the initial state ((F)/(E): 0.07 for  $\text{PO}_4\text{-P}$ , 0.06 for TP, 0.19 for  $\text{NH}_4\text{-N}$ , and 0.38 for TN;  $\text{PO}_4\text{-P}$  and  $\text{NH}_4\text{-N}$  are shown in Figure 4(c)–4(d)), and hanging GCA decreased these amounts to a lesser extent ((G)/(E): 0.43 for  $\text{PO}_4\text{-P}$ , 0.44 for TP, 0.55 for  $\text{NH}_4\text{-N}$ , and 0.62 for TN). Based on supplementary experiment (3), seawater brought about a larger nutrient release than freshwater ((I)/(H): 1.5 and 3.5; (K)/(J): 2.0 and 8.1 for  $\text{PO}_4\text{-P}$  and  $\text{NH}_4\text{-N}$ , respectively, at 30 days after the start; Figure 4(e)–4(f)). Supplementary experiment (4) showed that sand was more effective in reducing the nutrient release ((L)/(M): 2.1, 1.9, 11.9, and 4.3 in the oxic column; (N)/(O): 10.1, 6.0, 52.0, and 2.6 in the anoxic column for  $\text{PO}_4\text{-P}$ ,  $\text{NH}_4\text{-N}$ , TP, and TN, respectively, at 30 days after the start;  $\text{PO}_4\text{-P}$  and  $\text{NH}_4\text{-N}$  in Figure 4(g)–4(h)). Similar tendencies

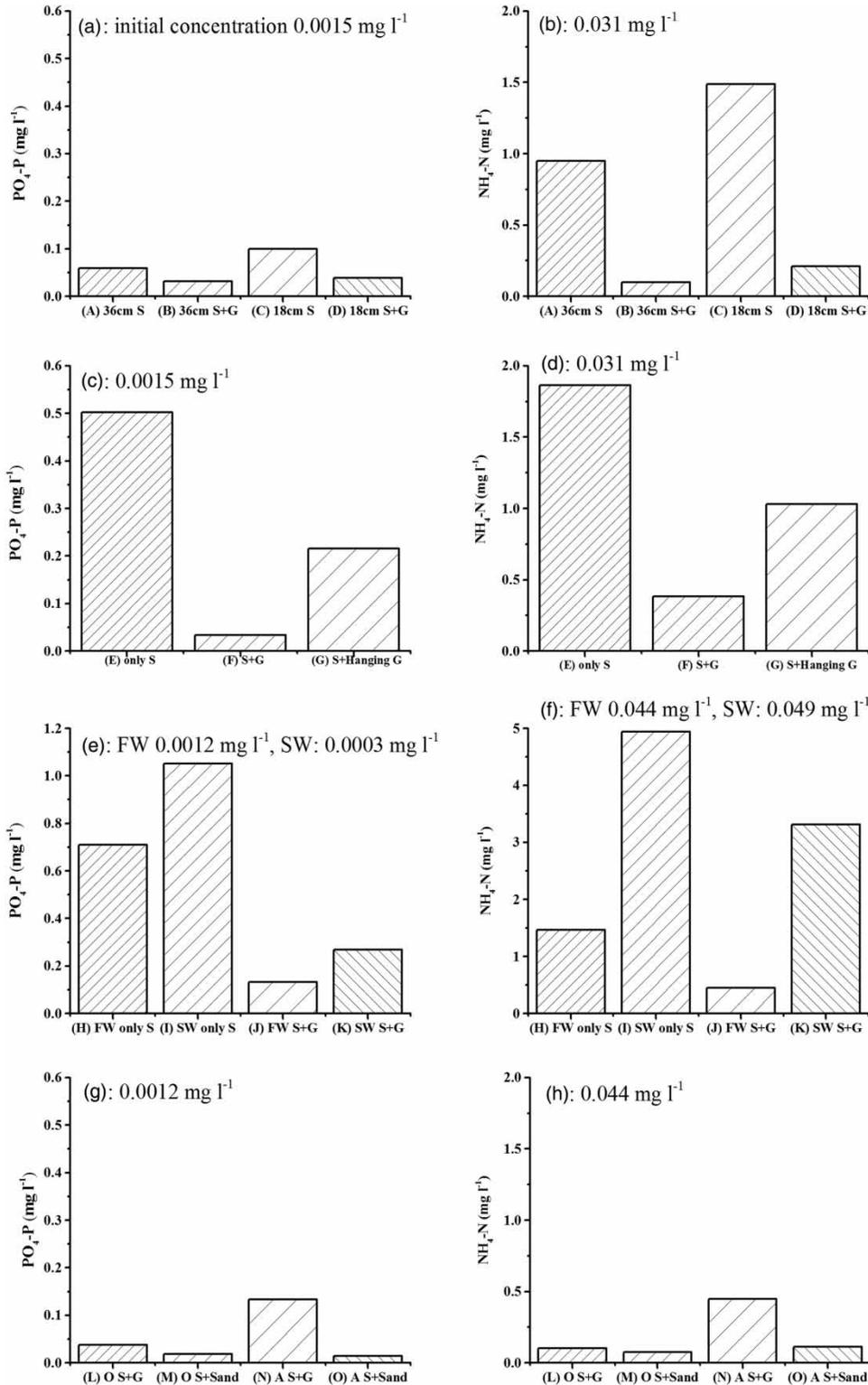
were also found at other incubation times in supplementary experiments (3) and (4).

#### Adsorption isotherm in supplementary experiment (5)

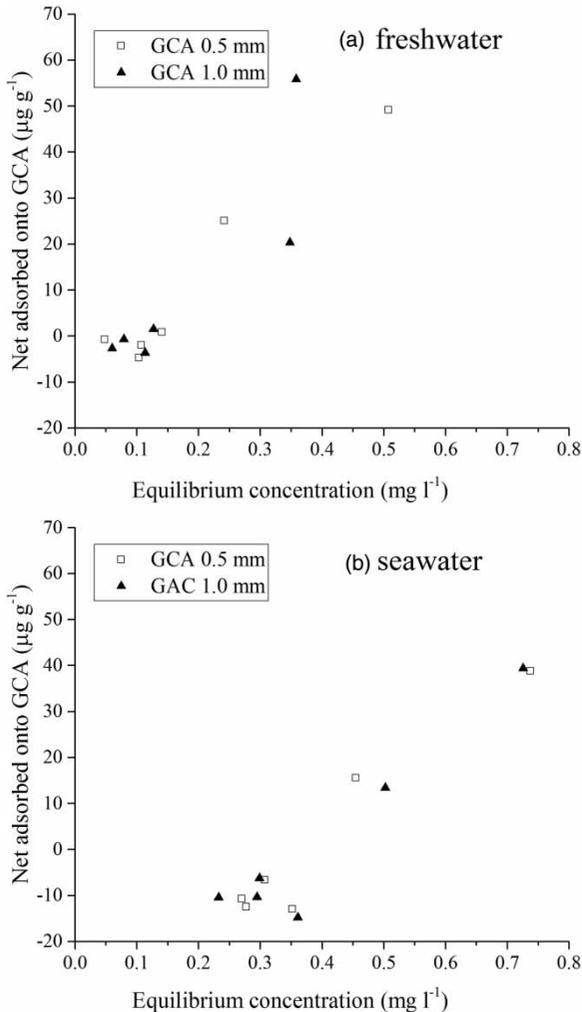
The relationship between the equilibrium  $\text{PO}_4\text{-P}$  in water and net adsorbed P on the GCA was determined as shown in Figure 5. A release of  $\text{PO}_4\text{-P}$  at a low  $\text{PO}_4\text{-P}$  concentration was observed and the threshold concentration between adsorption and desorption, which could be estimated as the equilibrium concentration at zero net adsorption onto GCA, was lower in freshwater compared with seawater (below  $0.1 \text{ mg l}^{-1}$  and  $0.4 \text{ mg l}^{-1}$  in freshwater and seawater, respectively). The mean diameter of GCA gave an insignificant difference in adsorption characteristics.

#### Calculation of TP and TN release rates in main experiment

The release rates of TP and TN were calculated for both the initial and intermediate periods (Table 4). The rates during the initial period indicated the speeds of the initial reaction in sediments and overlying water. Since nearly linear increases were observed during this period, the changes during approximately the first 15 days were used for the calculation of these rates. The concentrations at the start were excluded from the summer experiment because the influence of the initial disturbance on sediments remained in the vessels (e.g. S3, S6). In contrast, the intermediate period expressed the condition after the DO concentration reached an approximately steady level. In the summer experiment, anoxic vessels showed maximum speeds of TP release during this period. In the case of TP, the rate in S4 (anoxic without GCA) during the intermediate period showed a much higher value ( $8.9 \text{ mg m}^{-1} \text{ d}^{-1}$ ) than the others (up to  $2.9 \text{ mg m}^{-1} \text{ d}^{-1}$ ), and this high rate continued for 100 days. The rates in the vessels with GCA (F2, F3, F5, F6 and F7) were rather high, but did not continue after the initial period. In the case of TN, the vessels without GCA showed higher rates (up to  $56.4 \text{ mg m}^{-1} \text{ d}^{-1}$ ) compared with those with GCA (up to  $23.9 \text{ mg m}^{-1} \text{ d}^{-1}$ ) in both the fall and summer experiments. In general, the values of sediment oxygen demand (SOD) were high in the vessels without GCA.



**Figure 4** PO<sub>4</sub>-P and NH<sub>4</sub>-N concentrations observed at the ends of supplementary experiments (the initial concentrations also shown): (a) and (b) supplementary experiment (1) concerning different water depths; (c) and (d) supplementary experiment (2) comparing the physical and chemical effects; (e) and (f) supplementary experiment (3) comparing freshwater and seawater at 30 days after the start in anoxic columns; (g) and (h) supplementary experiment (4) comparing GCA and sand at 30 days after the start.



**Figure 5** | Relationship between equilibrium  $\text{PO}_4\text{-P}$  concentration and net adsorbed phosphorus on GCA at 28 days after the start. The net adsorbed phosphorus is the adsorbed minus the desorbed amount calculated based on the change in the  $\text{PO}_4\text{-P}$  concentration in the water phase. (a) freshwater (b) seawater.

## DISCUSSION

### Observed nutrient flux from sediment

Supplementary experiment (1) indicated a roughly reverse proportion between released nutrient concentration and water depth, suggesting the nearly constant flux of the sediments. Because almost all of the ratios ((C)/(A) and (D)/(B)) were, however, less than 2, the amount of releasable nutrients in the sediments and/or adsorbed on sediments or GCA as shown in Figure 5

probably affects the amount of released nutrients. Thus, we focus hereafter on the flux from the sediments, but the fluxes in the field might be higher than the fluxes determined in this experimental study because the water depths in the field are generally greater than those in the experimental columns.

Fukushima *et al.* (2010) reported that the nutrient release rates in Lake Kasumigaura were  $2.0 \pm 1.9 \text{ mg m}^{-2} \text{ d}^{-1}$  for TP and  $20.0 \pm 23.2 \text{ mg m}^{-2} \text{ d}^{-1}$  for TN by calculating the change in the overlying water concentrations while considering the water advection. Based on the vertical profiles of the interstitial nutrient concentrations, the nutrient release rates were estimated to be 3 and  $60 \text{ mg m}^{-2} \text{ d}^{-1}$  for TP and TN, respectively (Imai 2007). Our observed release rates in vessels without GCA were close to these values, indicating that the experiments roughly described the nutrient situation in Lake Kasumigaura. In addition, the estimated values of SOD for the sediment samples taken in Lakes Kasumigaura and Kitaura were determined to be  $0.46\text{--}0.60 \text{ g m}^{-2} \text{ d}^{-1}$  using a column chamber experiment (Komatsu *et al.* 2010). Bouffard *et al.* (2013) reported that the magnitude of SOD in mesotrophic Lake Erie was  $0.41 \pm 0.07 \text{ g m}^{-2} \text{ d}^{-1}$  based on the vertical profiles of DO in the water column. These rates were a little higher than our observed rates (Table 4), but the order of SOD was the same. There was a possibility of a slight oxygen supply to the anoxic vessels through the covers.

As shown in Table 4, the nutrient release fluxes in the vessels with GCA were smaller than those in the vessels without GCA, except for TP in the fall experiment. This exception seemed to be a minor matter because the TP amount released from the vessel without GCA under anoxic conditions in the summer experiment was much higher than those for the other vessels. The depths of the GCA (5 cm or 15 cm) insignificantly affected the fluxes (F2 vs F3, F6 vs F7, S5 vs S7), suggesting that a depth of 5 cm is sufficient to reduce the nutrient flux for a half year. Although the application of GCA to real lakes could suppress the sediment resuspension through wind waves, the settled sediments overlying on the GCA however brought about higher nutrient fluxes (S3 and S6), indicating that the deposition of resuspended sediments on GCA probably reduced its effect on the nutrient release from the sediments.

**Table 4** | TP and TN release rates ( $\text{mg m}^{-2} \text{d}^{-1}$ ) and sediment oxygen demand (SOD:  $\text{mg m}^{-2} \text{d}^{-1}$ )

	TP release rate		TN release rate		SOD Initial <sup>*1</sup>
	Initial <sup>*1</sup>	Intermediate <sup>*2</sup>	Initial <sup>*1</sup>	Intermediate <sup>*2</sup>	
F1 Oxic no GCA	1.6	1.0	56.4	13.2	
F2 Oxic 5 cm GCA	2.9	0.3	20.0	9.7	
F3 Oxic 15 cm GCA	2.4	0.1	23.9	7.7	
F4 Oxic no-sed	0.9	0.7	6.7	0.8	
F5 Anoxic no GCA	1.8	0.1	52.0	2.9	208
F6 Anoxic 5 cm GCA	1.8	0.8	12.3	6.1	82
F7 Anoxic 15 cm GCA	1.4		14.9	4.1	90
	Initial <sup>*3</sup>	Intermediate <sup>*4</sup>	Initial <sup>*3</sup>	Intermediate <sup>*4</sup>	Initial <sup>*5</sup>
S1 Oxic no GCA	1.1	0.5	23.0	1.6	46
S2 Oxic 10 cm GCA	0.2	0.8	16.2		
S3 Oxic 10 cm GCA + RS		0.2			
S4 Anoxic no GCA	2.3	8.9	26.8	19.2	255
S5 Anoxic 10 cm GCA			3.2	9.2	187
S6 Anoxic 10 cm GCA + RS		1.6		13.6	227
S7 Anoxic 5 cm GCA	0.1	0.3	6.0	9.3	226

Blanks indicate changes in the decrease during the period. Initial<sup>\*1</sup>: 0 days after the start to 15 days after the start; Intermediate<sup>\*2</sup>: 31 days to 44 days; Initial<sup>\*3</sup>: 2 days to 14 days; Intermediate<sup>\*4</sup>: 31 days to 45 days, Initial<sup>\*5</sup>: 0 days to 14 days.

### Mechanism of the suppression of nutrient release and comparison with other materials

Based on supplementary experiment (2), the hanging GCA had the effect of reducing the nutrient flux, but the degree of the reduction was smaller than that of the GCA overlying on sediments. It was considered that the hanging GCA had only a chemical effect, e.g. adsorption on the GCA or precipitation as calcium phosphate, while the overlying GCA had both chemical and physical effects on nutrient release. Regarding the ratios of  $((E)-(G))/((G)-(F))$ : chemical vs physical) for several nutrient forms ( $\text{PO}_4\text{-P}$ : 1.6,  $\text{NH}_4\text{-N}$ : 1.3, TP: 2.4, and TN: 1.6), the chemical effect of GCA was similar to its physical effect.

Under seawater conditions, phosphate adsorption by GCA and/or precipitation as calcium phosphate were considered to be the cause of P reduction based on the adsorption isotherm between GCA and phosphate (Asaoka & Yamamoto 2010). This previous study showed the threshold phosphate concentration over which phosphate was removed to be  $0.054 \text{ mg l}^{-1}$ , but the figure there

(Figure 4 in Asaoka & Yamamoto 2010) indicated that negligible adsorption or release occurred below  $0.3 \text{ mg l}^{-1}$ . In our experiment, the threshold concentrations were  $0.1 \text{ mg l}^{-1}$  for freshwater and  $0.4 \text{ mg l}^{-1}$  for seawater, which were close to the above-mentioned values. The low ionic conditions in freshwater might be the reason for the lower threshold concentration, suggesting the usefulness of GCA in a freshwater environment. In addition, hydrolysis of calcium salts such as  $\text{CaCO}_3$  and a subsequent increase in pH are the causes of the suppression of sulfate-reducing bacteria and remediation of coastal marine sediments (Asaoka *et al.* 2009). For freshwater sediments, this factor might be negligible due to the much lower concentration of sulfate in the water. Further, a release of silicon from GCA was considered to be another cause of the remediation of the coastal environment, but the concentrations of dissolved silicon were lower in vessels with GCA compared with vessels without GCA. The release of silicon from sediments was suppressed by GCA that covered the sediments.

Supplementary experiment (4) indicated that sand was more effective for the suppression of nutrient release

compared with GCA. The physical influence obtained through capping the sediments is expected to be larger for sand compared with GCA probably due to a lower level of mixing through the pores. In addition, the concentrations of calcium in columns with sand were comparable to those in columns with GCA (ratios between calcium at 30 days after the start and the initial column level: 2.2, 1.8, 1.3, and 1.7 for (L), (M), (N), and (O), respectively), suggesting that calcium was released from the sand and that calcium phosphate was subsequently precipitated.

There are several materials, e.g. Phoslock™, modified zeolite, alum, calcite, etc., which are used for P-inactivation to reduce internal nutrient loads (Zamparas & Zacharias 2014). They are usually applied as a slurry or as granules, and the efficiency of P reduction is rather high with coverage at a thickness on the mm-order. In addition, their phosphate adsorption capacity (10.5, 12.7, 12–13.8, and 6.4 mgP g material<sup>-1</sup> for Phoslock™, modified zeolite, alum, and calcite, respectively) is significantly higher than that of GCA (Figure 5). This is because they are pure or nearly pure chemicals.

### Possibility of GCA application in real lakes

Although the percentage of coal in world electricity production is expected to decrease from 41% in 2013 to 30% in 2040 due to the increase in renewable energy sources (wind, solar, etc.), the amount of electricity production by coal will not change largely during this period (IEA 2015), indicating the importance of reusing coal ash. The GCA used in this study was produced by mixing fly ash with cement as a binder through the granulation process. Generally, GCA has been used only for road beds, as a construction material, and as a coarse aggregate for concrete. Therefore, new applications utilizing by-products from coal thermal power plants are expected to promote recycling and waste reduction (Asaoka *et al.* 2009). In this context, GCA application to lake sediments as a remediation material is desired.

A positive effect on the suppression of nutrient release from anoxic sediments was confirmed by our experiments. The targets of GCA application were lakes with high P concentration (substantially higher than 0.1 mg l<sup>-1</sup>) due to the release of P from sediments. While the efficiency of GCA at a 5-cm thickness was observed for a half year, there is a

possibility that the reducing capacity can be lowered over time through the overlying of resuspended sediments on the GCA in lakes where wind waves sometimes disturb the surface sediments. Considering the resuspended sediments on GCA, the application of GCA to less disturbable areas (probably deep and small water regions) is practical. On the other hand, the release of toxic heavy metals was also observed, indicating that the application of GCA to lakes can also have adverse consequences. The standard values for both drinking water and public waterbodies in Japan are 10, 3, 50, 10, and 10 for As, Cd, Cr (as hexavalent type), Pb, and Se, respectively. Based on Figures 2 and 3, and supplementary Figures (d) and (h) (available online), the concentrations of Pb and Se were always lower than the standards and a few samples just slightly exceeded the standards of As and Cr. In the case of Cd, the standard was particularly exceeded in the fall experiment regardless of the oxic or anoxic conditions. Although the maximum concentration of Cd observed in our experiments was about double the standard concentration, the expected Cd concentration in real lakes with greater depths would be smaller than our observed concentrations. Further research is needed on the release of Cd from GCA, and a new technology for reducing the release of heavy metals (e.g. addition of additive) should be developed. By the way, the increase in Ca<sup>2+</sup> and the decrease in Mg<sup>2+</sup> probably have minor influences on lake chemistry and ecosystem because the changes in lake concentrations are expected to be rather small.

### CONCLUSIONS

The effectiveness of GCA suppressing nutrient release from sediments was examined for freshwater environments using large-volume vessels. The ability of GCA to reduce the nutrient fluxes in eutrophic lakes and the mechanism by which it does so were investigated. Also, this application of GCA was compared with its application to seawater and with other materials. In addition, the release of toxic chemicals (e.g., heavy metals) was investigated. Its applicability seems fairly promising, but further research e.g., the development of technology for reducing the release of heavy metals, and the consideration of its use from the view of recycling and waste reduction, are necessary before GCA can be utilized in a freshwater environment.

## ACKNOWLEDGEMENT

This research was supported in part by Grants in Aid for Scientific Research (No. 26281039) from the Ministry of Education, Culture, Sport, Science and Technology (MEXT), Japan.

## REFERENCES

- Asaoka, S. & Yamamoto, T. 2010 Characteristics of phosphate adsorption onto granulated coal ash in seawater. *Marine Pollution Bulletin* **60** (8), 1188–1192.
- Asaoka, S., Yamamoto, T., Yoshioka, I. & Tanaka, H. 2009 Remediation of coastal marine sediments using granulated coal ash. *Journal of Hazardous Materials* **172** (1), 92–98.
- Asaoka, S., Hayakawa, S., Kim, K.-H., Takeda, K., Katayama, M. & Yamamoto, T. 2012 Combined adsorption and oxidation mechanisms of hydrogen sulfide on granulated coal ash. *Journal of Colloid and Interface Science* **377**, 284–290.
- 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. *Chemical Engineering Journal* **254**, 531–537.
- Bormans, M., Maršálek, B. & Jančula, D. 2016 Controlling internal phosphorus loading in lakes by physical methods to reduce cyanobacterial blooms: a review. *Aquatic Ecology* **50** (3), 407–422.
- Bouffard, D., Ackerman, J. D. & Boegman, L. 2013 Factors affecting the development and dynamics of hypoxia in a large shallow stratified lake: hourly to seasonal patterns. *Water Resources Research* **49** (5), 2380–2394.
- Fukuma, H., Hibino, T., Yamamoto, T. & Saito, T. 2009 Restoration of water environment by covering granulated coal ash in brackish-water Lake Nakaumi, Japan. *Journal of Japan Society of Civil Engineers (Coastal Engineering)* **B2-65** (1), 1026–1030.
- Fukushima, T. & Arai, H. 2015 Regime shifts observed in Lake Kasumigaura, a large shallow lake in Japan: analysis of a 40-year limnological record. *Lakes & Reservoirs: Research & Management* **20** (1), 54–68.
- Fukushima, T., Kamiya, K., Onda, Y., Imai, A. & Matsushige, K. 2010 Long-term changes in lake sediments and their influences on lake water quality in Japanese shallow lakes. *Fundamental and Applied Limnology* **177** (3), 177–188.
- Galvez-Cloutier, R., Leroueil, S., Allier, D., Locat, J. & Arsenault, S. 2006 A combined method: precipitation and capping, to attenuate eutrophication in Canadian lakes. In: *Contaminated Sediments: Evaluation and Remediation Techniques* (M. Fukue, K. Kita, M. Ohtsubo & R. Chaney, eds), STP1482, ASTM International, West Conshohocken, PA, USA, pp. 232–239.
- Havens, K. E., Fukushima, T., Xie, P., Iwakuma, T., James, R. T., Takamura, N., Hanazato, T. & Yamamoto, T. 2001 Nutrient dynamics and the eutrophication of shallow lakes Kasumigaura (Japan), Donghu (PR China), and Okeechobee (USA). *Environmental Pollution* **111** (2), 263–272.
- IEA 2015 *World Energy Outlook*. OECD/IEA, Paris, France.
- Imai, A. 2007 Evaluation on the lake environment and scenario-planning for its restoration based on linkages among reactivity and chemical composition of organic matter. *Report Special Research National Institute for Environmental Studies SR-78*, 1–43 (in Japanese).
- Kamiya, K., Fukushima, T., Ouchi, T. & Aizaki, M. 2017 Phosphorus budgetary analysis of sediment–water interface in a short-term anoxic condition in shallow Lake Kasumigaura, Japan. *Limnology* **18** (1), 131–140.
- Kido, K., Saito, T., Uotani, R., Kuwabara, T. & Aizaki, M. 2014 Estimate of the efflux of N·P·S from sediments in dredging hollow in Lake Nakaumi and effect of sand capping with granulated coal ash. *Journal of Japan Water Society on Water Environment* **37** (3), 71–77 (in Japanese with English abstract).
- Kim, K., Hibino, T., Yamamoto, T., Hayakawa, S., Mito, Y., Nakamoto, K. & Lee, I.-C. 2014 Field experiments on remediation of coastal sediments using granulated coal ash. *Marine Pollution Bulletin* **83** (1), 132–137.
- Komatsu, N., Ishii, Y., Watanabe, K., Homma, T. & Kitazawa, D. 2010 Field observation and analyses of oxygen-deficient water mass in Lake Kasumigaura. *Annual Journal of Hydraulic Engineering, JSCE* **54**, 1399–1404 (in Japanese with English abstract).
- O’Neil, J. M., Davis, T. W., Burford, M. A. & Gobler, C. J. 2012 The rise of harmful cyanobacteria blooms: the potential roles of eutrophication and climate change. *Harmful Algae* **14**, 313–334.
- Schindler, D. W., Carpenter, S. R., Chapra, S. C., Hecky, R. E. & Orihel, D. M. 2016 Reducing phosphorus to curb lake eutrophication is a success. *Environmental Science & Technology* **50** (17), 8923–8929.
- Yamamoto, T., Harada, K., Kim, K. H., Asaoka, S. & Yoshioka, I. 2013 Suppression of phosphate release from coastal sediments using granulated coal ash. *Estuarine Coastal and Shelf Science* **116**, 41–49.
- Yamamoto, T., Kim, K. H. & Shirono, K. 2015 A pilot study on remediation of sediments enriched by oyster farming wastes using granulated coal ash. *Marine Pollution Bulletin* **90** (1–2), 54–59.
- Zamparas, M. & Zacharias, I. 2014 Restoration of eutrophic freshwater by managing internal nutrient loads. A review. *Science of the Total Environment* **496**, 551–562.