

## Effects of three iron material treatments on hydrogen sulfide release from anoxic sediments

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### ABSTRACT

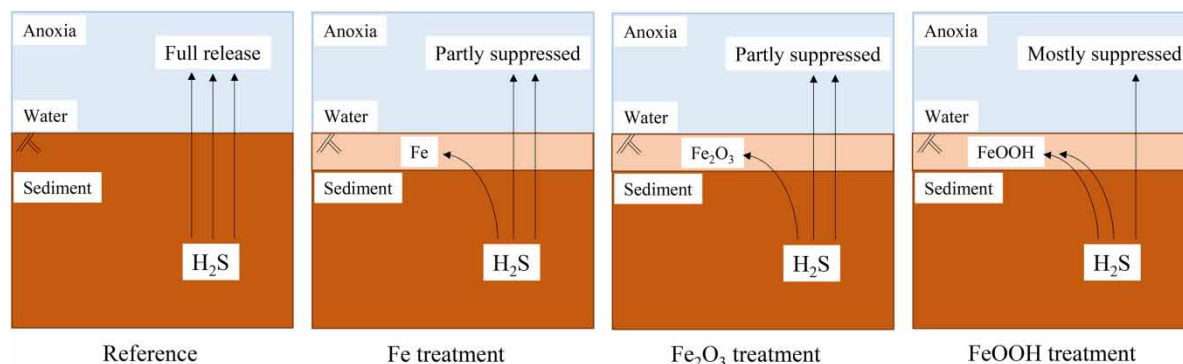
In eutrophic coastal regions, hydrogen sulfide ( $H_2S$ ) is a harmful material released from sediments under anoxic conditions. To suppress its release, we conducted laboratory experiments and assessed the impacts of treatment with three iron materials (Fe,  $Fe_2O_3$ , and FeOOH), focusing on the area-specific  $H_2S$  release rate. These materials qualitatively exhibited a substantial suppression of  $H_2S$  release; however, smaller treatment levels ( $<150 \text{ mmol m}^{-2}$ ) were ineffective. FeOOH exhibited the best performance, followed by  $Fe_2O_3$ , and Fe. These differences were likely caused by variations in the oxidation or reduction potential of the materials and their reaction rates with  $H_2S$ . A simplified model suggested that the required minimum  $Fe^{2+}$  concentration was determined using the  $H_2S$  diffusivity, reaction rate constant, and treatment penetration depth. As the former two are physical constants, the latter must control the  $H_2S$  release rate. Iron materials were experimentally confirmed to persist for over three weeks, and the effective treatment level was theoretically estimated as being capable of suppressing  $H_2S$  release for more than a year. Our results will contribute to coastal environmental management and particularly benefit port authorities who manage enclosed and eutrophicated harbors and navigation channels where slag application should be avoided.

**Key words:** Iron material treatment, sediment, sulfide release, suppression effect

### HIGHLIGHTS

- The ability of three iron materials to suppress  $H_2S$  release from anoxic sediment was tested.
- FeOOH showed the best performance, followed by  $Fe_2O_3$ , and Fe.
- The oxidation–reduction potential was increased by FeOOH treatment but decreased by Fe treatment.
- The treatment penetration depth was a primary parameter controlling  $H_2S$  release.

### GRAPHICAL ABSTRACT



## INTRODUCTION

Hydrogen sulfide ( $\text{H}_2\text{S}$ ) is toxic to many coastal organisms (Vismann 1996; Sugahara *et al.* 2016). It is a byproduct of anaerobic metabolism and is produced via sulfate reduction under anaerobic conditions, such as those with a redox potential of  $-100$  mV or below (Devai & DeLaune 1995). In coastal regions, it is released from anoxic sediments experiencing continuous anoxia (Fossing *et al.* 2004). Among the various measures proposed to mitigate this issue (Gächter & Wehrli 1998; Azuma *et al.* 2017), treatment with iron materials is considered effective (Mortimer 1941; Ripl 1986; Canfield 1989; Giordani *et al.* 1996) because dissolved iron combines with  $\text{H}_2\text{S}$  and precipitates ferrous sulfide.

Slag, a byproduct of steelmaking, is typically used to develop biological assemblages on the seafloor (Chou & Fang 2005) or to suppress  $\text{H}_2\text{S}$  release from eutrophic sediments (Miki *et al.* 2013). Although the use of slag is a widely accepted practice, there are several concerns associated with it, including the release of notable levels of heavy metals from the slag that can lead to water pollution and other environmental problems (Lim *et al.* 2016). Moreover, it can result in marked pH augmentations; in addition, the adhesion of slag lumps by precipitated calcium carbonate – owing to calcium release from the slag – can have negative impacts on ecosystems (Asaoka *et al.* 2013).

This suggests that other iron materials that have fewer undesirable properties should be used to avoid these issues. However, to the best of our knowledge, such materials have rarely been tested as alternatives to slag. Kanaya & Kikuchi (2009) reported that the application of pure iron powder to sediment cores from a brackish lake formed insoluble iron sulfide and effectively suppressed the release of  $\text{H}_2\text{S}$  at high concentrations. Similarly, a few studies have also explored the application of iron granules. For example, Yin *et al.* (2018) applied iron granules to mitigate sedimentary  $\text{H}_2\text{S}$  release. Meanwhile, Sun *et al.* (2019) reported that iron granules could be reused four times during a 293-d trial and their overall sulfide removal capacity was at least 920 mg S/g Fe. However, the granules require regeneration by separating them from the sediment as well as re-oxidation, both of which are costly and time-consuming.

Such studies primarily focused on the capacity of iron to bind  $\text{H}_2\text{S}$ ; for instance, they focused on the stoichiometric ratio of Fe:S (Yin *et al.* 2018). However, as binding effects should be kinetically evaluated relative to the area-specific  $\text{H}_2\text{S}$  release rate, the area-specific amounts of iron compounds and the area-specific release rate must also be compared. In addition, the differences in the reactivities and oxidation potentials of various iron compounds are important factors. Therefore, in this study, we used laboratory experiments to assess the performance of three different iron materials (pure iron, Fe; ferric oxide,  $\text{Fe}_2\text{O}_3$ ; and ferric oxyhydroxide,  $\text{FeOOH}$ ) as inhibitors of  $\text{H}_2\text{S}$  release from anoxic sediments.

## MATERIALS AND METHODS

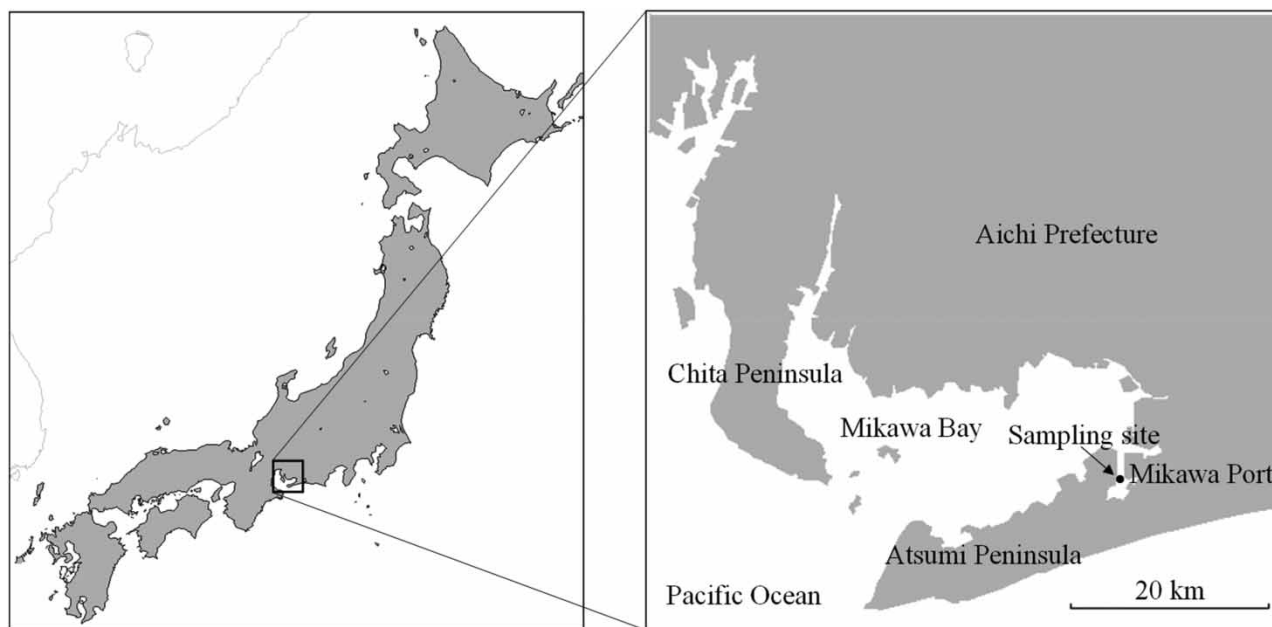
### Site description

Mikawa Bay is a eutrophic enclosed bay (604 km<sup>2</sup> in area, 9.2 m mean depth) in Aichi Prefecture in central Japan. It is surrounded by the Chita and Atsumi Peninsulas (Ishida & Kuroda 2007) and connected to the Pacific Ocean through a 9.4 km-wide mouth, which is the only source of seawater exchange (Hafeez *et al.* 2021; Figure 1). The bathymetry of the bay is bowl-shaped with a maximum depth of  $\sim 20$  m near its center, which further restricts water exchange with the Pacific Ocean. Weak vertical mixing results in the depletion of dissolved oxygen in the bottom layer during summer. Mikawa Port is in the innermost part of the bay and is accessible through several navigation channels with significantly eutrophic sediments that are considered important sources of anoxia and  $\text{H}_2\text{S}$  release. Therefore, improvements in the local sediment quality are desirable.

### Sampling and experimental setup

Intact sediment cores of approximately 30-cm thickness were collected from a navigation channel using Plexiglas cores (10-cm diameter, 50-cm height) (34°42.7720'N, 137°18.2960'E,  $\sim 12$ -m depth) by scuba diving to the floor of the bay. Furthermore, water was collected from near the sampling sites. Nine sediment cores were sampled from the same site, within a range of approximately 5 m; they served as experimental cores and were not disturbed.

In the present study, three different experiments were conducted that differed with respect to the duration of the incubation period and the amount of iron material added to the sediment cores. Experiment 1 included 5 d of incubation with sufficient iron material treatment (i.e., the amount of iron material was not based on the expected  $\text{H}_2\text{S}$  release). Experiment 2 also included 5 d of incubation, but the amount of iron material that was added was calibrated based on the expected  $\text{H}_2\text{S}$  release. In contrast, Experiment 3 had a 3-week incubation period. Furthermore, each experiment had three different



**Figure 1** | Location of Mikawa Bay and sampling site.

experimental conditions based on the type and amount of iron material used. Of the nine cores used for each experiment, three were used as references (labeled 1A-1, 1A-2, and 1A-3 in Experiment 1; 2A-1, 2A-2, and 2A-3 in Experiment 2; and 3A-1, 3A-2, and 3A-3 in Experiment 3), three were treated with different amounts of FeOOH (labeled 1C-1, 1C-2, and 1C-3 in Experiment 1; 2C-1, 2C-2, and 2C-3 in Experiment 2; and 3C-1, 3C-2, and 3C-3 in Experiment 3), and the remaining three were treated with different amounts of Fe in Experiments 1 and 2 (labeled 1B-1, 1B-2, and 1B-3 in Experiment 1 and 2B-1, 2B-2, and 2B-3 in Experiment 2). In Experiment 3, they were treated with Fe<sub>2</sub>O<sub>3</sub> (labeled 3D-1, 3D-2, and 3D-3). The sediment cores were immediately transported to the laboratory and placed in an experimental room where the *in-situ* temperature of the sampling site was maintained. The water samples, which were collected from the sampling site, were treated to minimize the effects of biochemical reactions during the incubation experiments. The water was first filtered using cellulose acetate membrane filters (0.45 μm pore size, 293 mm diameter, C045A293C, Advantec Co., Ltd, Tokyo, Japan), bubbled with N<sub>2</sub> gas to minimize the oxygen concentration, and carefully poured into the core to avoid sediment suspension (Inoue *et al.* 2017). Thereafter, the iron materials were added to the cores in varying amounts (Table 1), and the cores were sealed to make them air-tight. The cores were then installed in a water bath to maintain the ambient temperature of the relevant sampling site. The experiments were conducted after 1 d of pre-incubation, which was inferred to be sufficient for achieving *in-situ* conditions (e.g., Glud *et al.* 1999).

The water overlying the sediment was agitated using a fluororesin propeller (PTFE straight-blade, Model No. FLSPI, As One Co., Ltd, Osaka, Japan) and a brushless motor (BMU230A-15-2, Oriental Motor Co., Ltd, Tokyo, Japan) to ensure that it was mixed thoroughly and to control the hydrodynamic conditions in the cores (Inoue & Nakamura 2009). The propeller and the motor were attached to a vacuum stirrer using a magnetic drive system (PTFE magnet vacuum stirring device, Model No. F-24/40, As One Co., Ltd, Osaka, Japan) to prevent exposure of the water to air. The rotation speed was set at 30 rpm, and no resuspension of the sediment particles was observed. During incubation, the cores were shaded using a blackout curtain to avoid light exposure. The oxygen concentrations in the overlying water were measured at 1-h intervals using a dissolved oxygen meter (WA-2017SD, FUSO, Tokyo, Japan) to confirm anoxic conditions (Figure 2).

The overlying water was sampled using a tube (4-mm inner diameter, 6-mm outer diameter, LMT-55, Saint-Gobain K.K., Tokyo, Japan) with the inlet placed ~50 mm above the sediment surface (not exposed to the air, Figure 2), and the portion of sampled water was immediately filtered using a disposable filter (pore size 0.45 μm, Minisalt SM16555 K, Sartorius Co., Goettingen, Germany). Part of the filtered water sample was directly poured into a bottle containing a chromogenic reagent (N,N-dimethyl-p-phenylenediamine dihydrochloride solution) to stabilize the H<sub>2</sub>S and minimize oxidation in the sampled

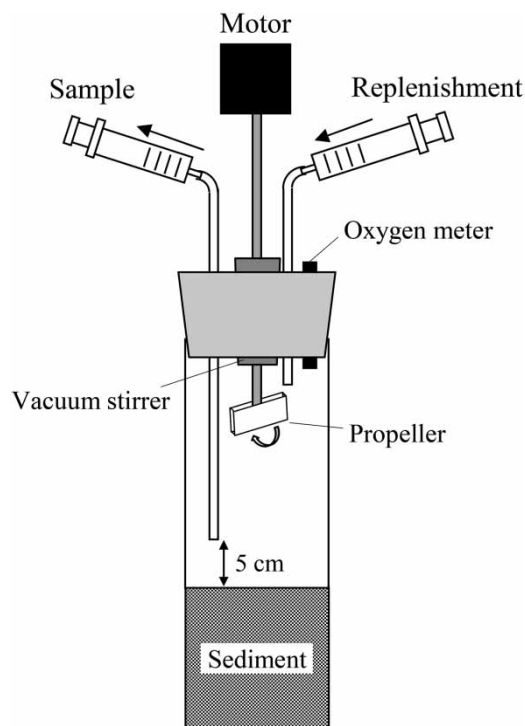
**Table 1** | Experimental conditions and H<sub>2</sub>S release rates

Experiment	Core	Iron material	Treatment amount (mmol)	H <sub>2</sub> S release rate (mmol m <sup>-2</sup> d <sup>-1</sup> )	Suppression rate relative to reference cores (%)	Average suppression rate (%)
1	1A-1	–	0	10.2	–	–
	1A-2	–	0	10.2	–	–
	1B-1	Fe	38.5	0.3	96.9	97.1
	1B-2	Fe	44.8	0.3	97.2	
	1B-3	Fe	81.2	0.3	97.3	
	1C-1	FeOOH	40.7	0.0	100.0	100
	1C-2	FeOOH	46.9	0.0	100.0	
	1C-3	FeOOH	85.5	0.0	100.0	
	2	2A-1	–	0	5.5	–
2A-2		–	0	4.9	–	–
2A-3		–	0	4.6	–	–
2B-1		Fe	0.56	5.3	–7.0	19.1
2B-2		Fe	1.13	4.8	3.7	
2B-3		Fe	2.18	2.0	60.6	
2C-1		FeOOH	0.60	5.8	–16.6	45.0
2C-2		FeOOH	1.22	1.4	72.9	
2C-3		FeOOH	2.26	1.1	78.6	
3	3A-1	–	0	16.5	–	–
	3A-2	–	0	13.8	–	–
	3A-3	–	0	25.2	–	–
	3C-1	FeOOH	63.0	1.2	93.7	89.6
	3C-2	FeOOH	63.0	0.5	97.5	
	3C-3	FeOOH	63.0	4.1	77.8	
	3D-1	Fe <sub>2</sub> O <sub>3</sub>	63.0	9.8	47.0	49.3
	3D-2	Fe <sub>2</sub> O <sub>3</sub>	63.0	10.7	42.4	
	3D-3	Fe <sub>2</sub> O <sub>3</sub>	63.0	7.7	58.5	

water. The remaining filtered and non-filtered samples were separately poured into acid-washed polypropylene bottles and stored at –25 °C until further chemical analyses. The H<sub>2</sub>S release rates from the sediment were calculated based on the increasing H<sub>2</sub>S concentration in the overlying water during incubation.

Immediately after the incubation period, one of the three sediment cores was arbitrarily selected from each experimental condition, and the oxidation–reduction potential (ORP) was measured by inserting an electrode directly into the sediment. From the remaining two sediment cores, six sediment layers – each 1.5 cm thick – were removed from the upper 9.0 cm of the cores to obtain vertical profiles based on the amount of H<sub>2</sub>S in the pore water and the sediment quality. These layers were placed in 100-mL containers. Of these samples, 100 mL was stored at –25 °C until further analysis for water content, loss of ignition, chemical oxygen demand, total nitrogen, total phosphorus, free sulfide, and acid volatile sulfide. The remaining samples were centrifuged in N<sub>2</sub>-filled tubes at 3,000 rpm for 10 min to separate out the pore water. The supernatant was filtered using a syringe and a disposable filter (pore size 0.45 µm, Saltrius, Minisalt SM16555 K) to avoid air exposure. These were also stored at –25 °C until further chemical analysis (Figure 3).

Prior to the H<sub>2</sub>S release experiments, a ferric chloride aqueous solution was boiled to evaporate the water and produce a half-dried residue that was used in Experiments 1 and 2. The residue was primarily FeOOH, with small portions of ferric chloride and Fe<sub>2</sub>O<sub>3</sub>. Hereafter, we refer to this residue simply as FeOOH.



**Figure 2** | Schematic view of a sediment core. The water overlying the sediment was agitated using a propeller at 30 rpm. The water sample was collected using a tube and the same amount of filtered and deoxidized water was replenished at the same time without exposing the sample to the air.

### Experiment 1: Five days of incubation with sufficient iron material treatment

This experiment was conducted by adding enough Fe or FeOOH to qualitatively confirm the effectiveness of the treatment over 5 d. These treatments produce  $\text{Fe}^{2+}$  by oxidizing Fe or reducing FeOOH and trap  $\text{H}_2\text{S}$ , thereby resulting in the suppression of  $\text{H}_2\text{S}$  release from the sediment. Assuming that equimolar iron and  $\text{H}_2\text{S}$  combine as follows (Fossing *et al.* 2004):



where 0.61 mmol iron would be required per core (cross-sectional area of  $78.5 \text{ cm}^2$ ) to suppress  $15.6 \text{ mmol m}^{-2} \text{ d}^{-1}$  (representative of the sampling site) of  $\text{H}_2\text{S}$  release for 5 d. Therefore, we added 38.5–81.2 mmol of Fe and 40.7–85.5 mmol of FeOOH to each core to represent a sufficient amount (Table 1), which was followed by 1 d of pre-incubation and subsequent incubation under anoxic conditions for 5 d. Triplicate cores were prepared for each condition and the experiment was conducted in the dark, except when the overlying water was sampled (every 12 h).

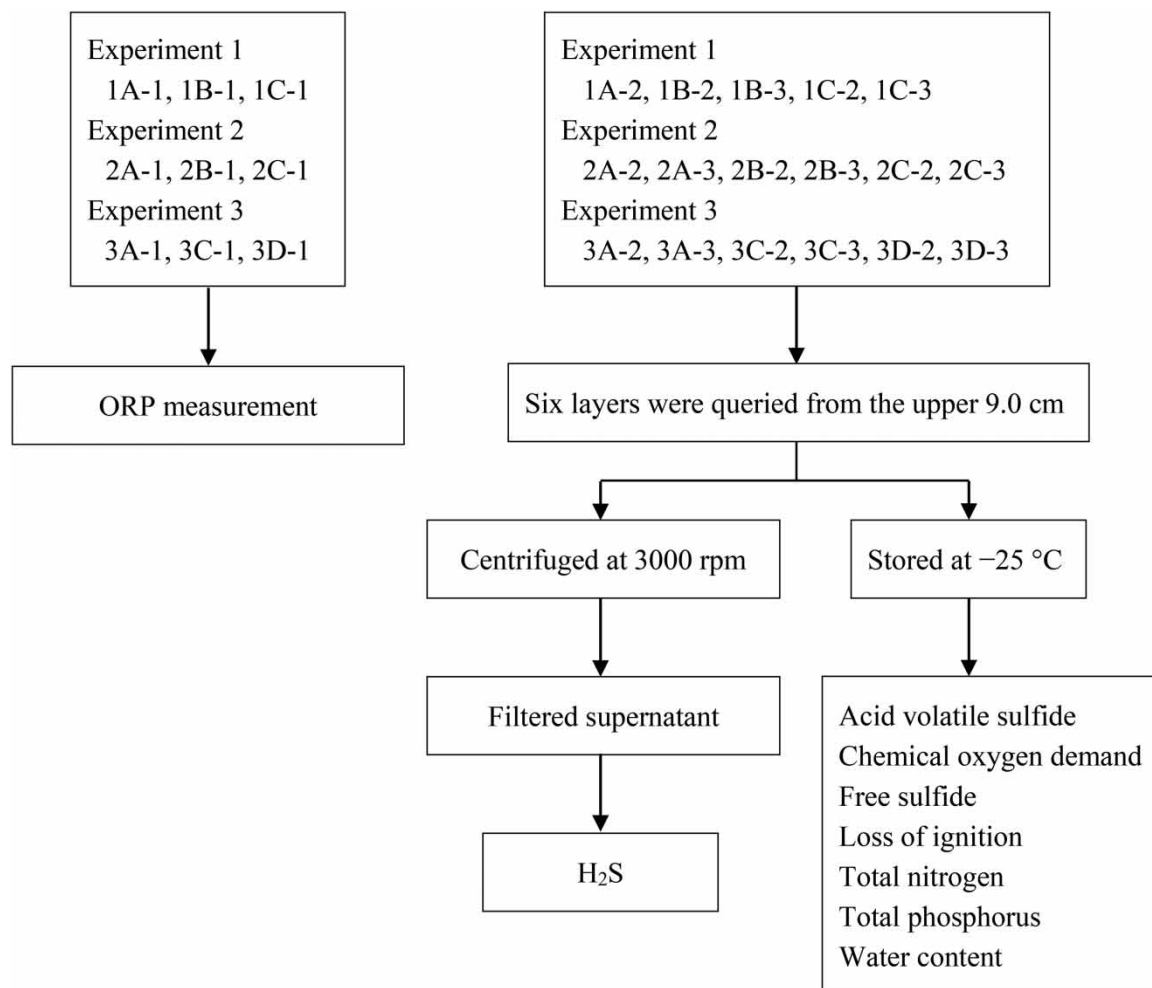
### Experiment 2: Five days of incubation with iron material treatment calibrated to expected $\text{H}_2\text{S}$ release

This experiment was conducted to study the effectiveness of adding a comparable amount of iron material calculated based on the expected  $\text{H}_2\text{S}$  release over 5 d.

Based on the stoichiometric estimation (Equation (1)), three levels of iron application were defined: 0.56, 1.13, and 2.18 mmol for Fe and 0.60, 1.22, 2.26 mmol for FeOOH. The core incubation conditions and overlying water sampling intervals were the same as those in Experiment 1.

### Experiment 3: Three weeks of incubation

This experiment was conducted to assess the three-week sustainability of iron material application and included the use of  $\text{Fe}_2\text{O}_3$  as an alternative treatment. This treatment also produced  $\text{Fe}^{2+}$  by reducing  $\text{Fe}_2\text{O}_3$  and trapped  $\text{H}_2\text{S}$ . Triplicate cores were prepared for each treatment and 63.0 mmol of  $\text{Fe}_2\text{O}_3$  and FeOOH (the same as in Experiment 1) were added to each core. In this case, a commercially available FeOOH (Cat. No. 16024-02, Kanto Chemical Co., Inc., Tokyo, Japan)



**Figure 3** | Analytical procedure adopted for each sediment core after incubation.

and the residue of the acid-pickling of steel products were used to provide  $\text{FeOOH}$  and  $\text{Fe}_2\text{O}_3$ , respectively. The core incubation conditions were same as in Experiments 1 and 2. The overlying water was sampled on the 1st, 2nd, 3rd, 4th, 7th, 14th, and 21st day after incubation commenced.

### Chemical analysis

$\text{H}_2\text{S}$  was analyzed in the overlying and pore water via the methylene blue method (Cline 1969) using a spectrophotometer (V-550, Jasco corporation, Tokyo, Japan). Divalent iron in the overlying and pore water was analyzed via the 1,10-phenanthroline method using the same spectrophotometer.

The sediment samples were analyzed for water content (gravimetric analysis following oven-drying at  $105^\circ\text{C}$ ), loss of ignition ( $600^\circ\text{C}$ , 2 h), chemical oxygen demand (titration after heating in a boiling water bath for 30 min), total nitrogen (indophenol blue absorptiometry after Kjeldahl decomposition), total phosphorus (molybdenum blue absorptiometry after decomposition by nitric acid/sulfuric acid mixture), free sulfide (titration after steam distillation), and acid volatile sulfide (201H, Gastech Co., Ltd, Kanagawa, Japan).

## RESULTS

Monitoring the oxygen concentration in the overlying water confirmed that all experiments were conducted under anoxic conditions. The sediment properties used in the experiments are listed in the Supplementary Material, Tables S1, S2, and S3.

## Experiment 1

As one of the reference cores in this experiment was broken and could not be used, only the results from the other cores are shown (Figure 4). 1A-1 and 1A-2 (references) showed substantial H<sub>2</sub>S release (average 10.2 mmol m<sup>-2</sup> d<sup>-1</sup>) while 1C-1, 1C-2, and 1C-3 (FeOOH) successfully suppressed H<sub>2</sub>S release. 1B-1, 1B-2, and 1B-3 (pure Fe) achieved ~97% suppression, allowing the release of only 0.29 mmol m<sup>-2</sup> d<sup>-1</sup> H<sub>2</sub>S on average.

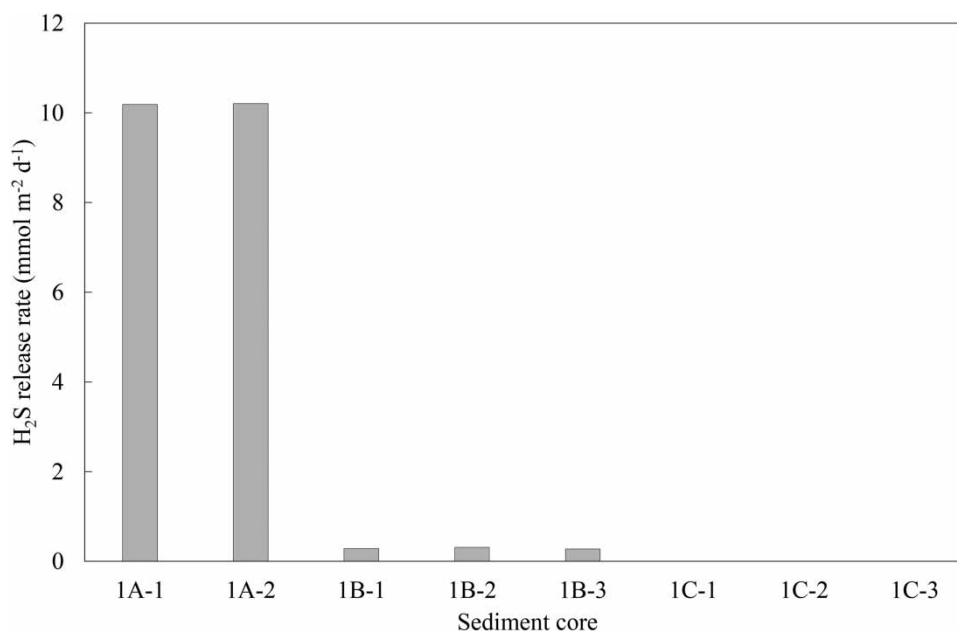
The ORP profiles of the FeOOH-treated cores shifted in a positive direction relative to the reference cores (Figure 5(a)), owing to the oxidation potential of FeOOH and the effects of its penetration to a depth of ~9 cm. Thus, FeOOH not only adsorbs H<sub>2</sub>S but also encourages oxic conditions in anoxic sediment. In contrast, pure Fe showed a negative effect on the ORP profile, possibly owing to its reduction potential. In this respect, treatment with pure Fe is unfavorable because it likely makes sedimentary environments more reductive.

The vertical H<sub>2</sub>S concentration profiles of the sediments after incubation (Figure 5(b)) showed that 1A-2 (reference) exhibited the highest concentration of the three cores in the surface layer (0–4.5 cm depth). 1B-2 (Fe) showed lower concentrations at these depths (0–4.5 cm) than the reference cores. Meanwhile, 1C-2 (FeOOH) showed the lowest values, seemingly owing to the chemical combination of H<sub>2</sub>S and the iron material. The H<sub>2</sub>S concentration in the deeper layer (6–9 cm depth) of 1A-2 (reference) was lower than those in the 3–4.5 cm layer and in the corresponding layer of 1B-2 (Fe).

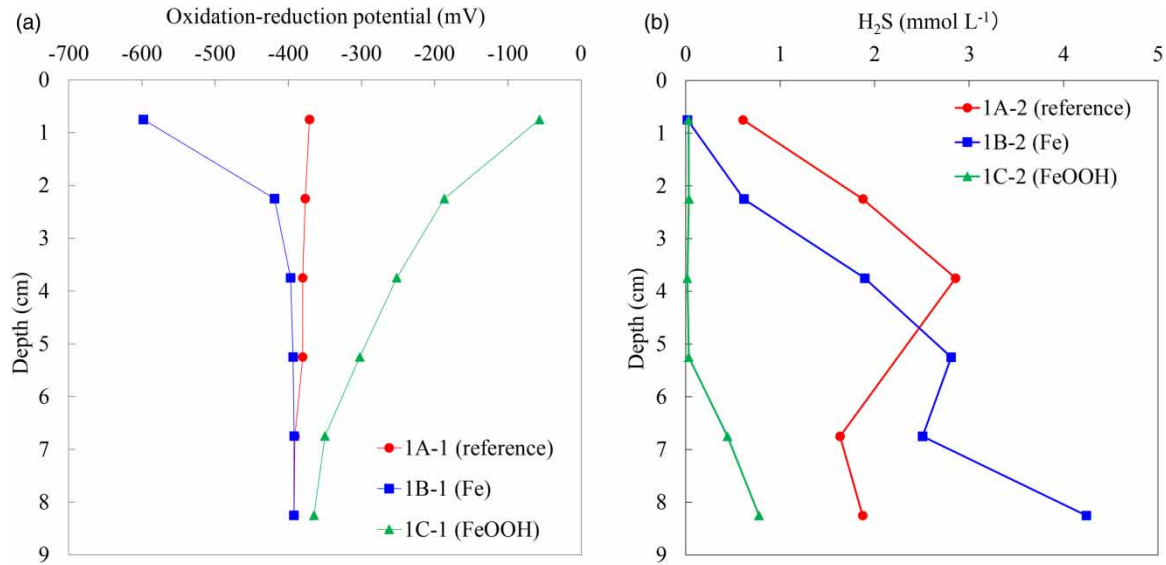
In addition, the acid volatile sulfide concentration in the 6–7.5 cm layer of 1A-2 (reference) was 0.027 mmol g<sup>-1</sup> dry sediment, which was lower than those in the 3–4.5 cm layer (0.063 mmol g<sup>-1</sup> dry sediment) of 1A-2 and the 6–7.5 cm layer of 1B-2 (0.079 mmol g<sup>-1</sup> dry sediment). Although the reason for this is currently unclear, there was likely a local inactive spot in the 6–7.5 cm layer of 1A-2. Regardless, this indefinite property does not qualitatively alter our conclusions as the H<sub>2</sub>S release rate was controlled by its profile within the first few centimeters of the sediment surface. We concluded that both Fe and FeOOH suppressed H<sub>2</sub>S release from sediments; however, FeOOH was preferable given its superior performance and the potential negative effects of pure Fe caused by its reductive nature.

## Experiment 2

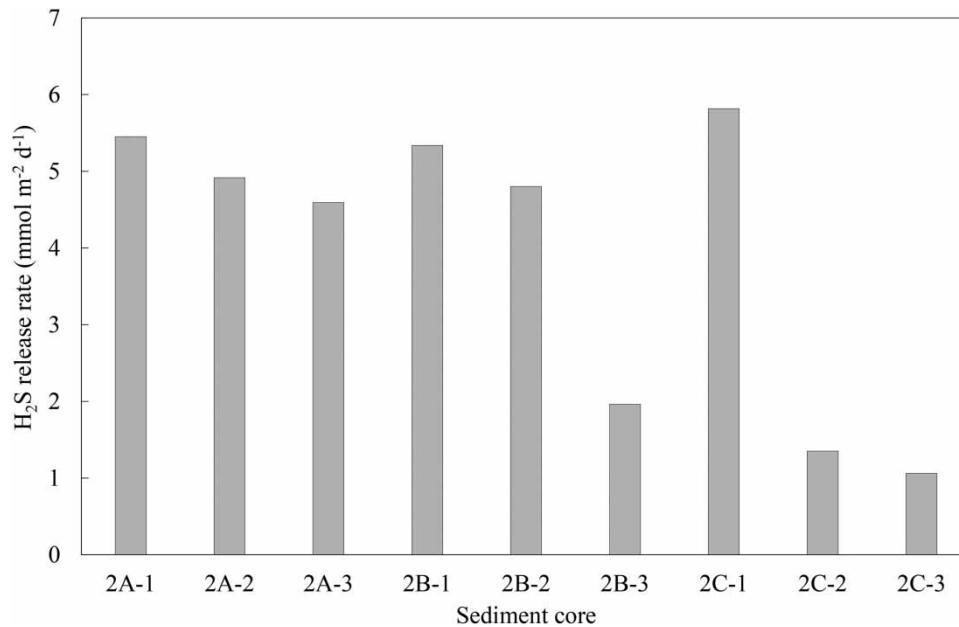
Overall, the H<sub>2</sub>S release rates were lower than those in Experiment 1 (Figure 6). 2A-1, 2A-2, and 2A-3 (reference) showed release rates of  $5.00 \pm 0.35$  mmol m<sup>-2</sup> d<sup>-1</sup>, which were ~49% of that of the reference cores in Experiment 1. 2B-1 and 2B-2 (0.56 mmol and 1.13 mmol pure Fe, respectively) and 2C-1 (0.60 mmol FeOOH) showed no suppressive effects on H<sub>2</sub>S release. In contrast, 2B-3 (2.18 mmol pure Fe), 2C-2 (1.22 mmol FeOOH), and 2C-3 (2.26 mmol FeOOH) showed substantial effects, suppressing 61, 73, and 79% of the expected release, respectively.



**Figure 4** | H<sub>2</sub>S release rates in Experiment 1, calculated from H<sub>2</sub>S concentrations in the overlying water throughout the incubation period.



**Figure 5** | Vertical profiles of (a) oxidation–reduction potential and (b) H<sub>2</sub>S concentration in the sediment after 5-d incubation in Experiment 1.



**Figure 6** | H<sub>2</sub>S release rates in Experiment 2.

The expected release was based on the values in the reference cores. This experiment successfully captured the occurrence threshold for H<sub>2</sub>S suppression. Moreover, when comparing 2B-2 and 2C-2 (in which almost the same amounts of pure Fe and FeOOH were added), FeOOH had a stronger effect than pure Fe, which supports the conclusion drawn from Experiment 1 that treatment with FeOOH is preferable for H<sub>2</sub>S release suppression.

Vertical ORP profiles showed no clear differences between the treatments (data not shown). However, the H<sub>2</sub>S concentration profile in the range of 0–4.5 cm in 2C-2 (FeOOH) showed some suppression compared to those in cores 2A-2 (reference) and 2B-2 (pure Fe). Therefore, the addition of small amounts of pure Fe and FeOOH (<150 mmol m<sup>-2</sup>) may have minor H<sub>2</sub>S suppression effects, and the threshold may alter depending on the type of material used. However, the



concentration of  $\text{H}_2\text{S}$  in the 4.5–7.5 cm layer of 2C-2 (FeOOH) was higher than those in 2A-2 (reference) and 2B-2 (pure Fe). This was similar to the results of Experiment 1. Although the reason for this finding is currently unclear, it could be due to heterogeneity in the deeper layers.

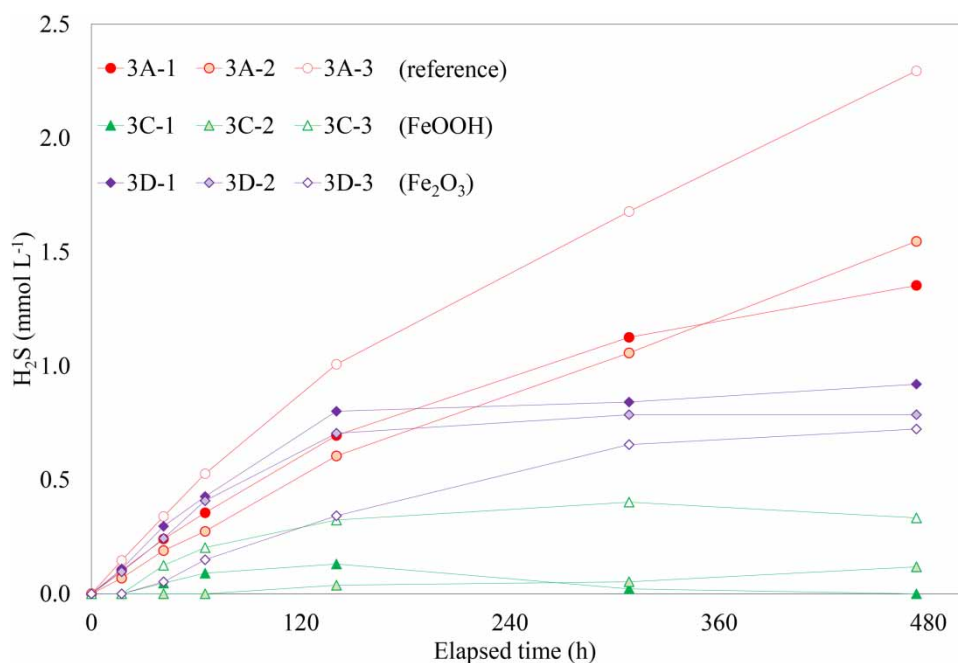
### Experiment 3

The 3A-1, 3A-2, and 3A-3 (reference) cores experienced a nearly constant increase in  $\text{H}_2\text{S}$  concentration in the overlying water, indicating constant  $\text{H}_2\text{S}$  release from the sediment (Figure 7). 3D-1 and 3D-2 ( $\text{Fe}_2\text{O}_3$ ) followed similar trends to the reference cores for the first 7 d, although their increase rates slowed thereafter, suggesting that  $\text{Fe}_2\text{O}_3$  treatments may require a certain amount of time to become reactive and start trapping  $\text{H}_2\text{S}$ . Generally,  $\text{Fe}_2\text{O}_3$  is regarded as an insoluble material that must be reduced to become soluble and reactive, thereby explaining the lag seen in 3D-1 and 3D-2. However, a slower increase of  $\text{H}_2\text{S}$  concentration was observed in 3D-3 for reasons that remain unclear, as all three cores were treated in the same manner.

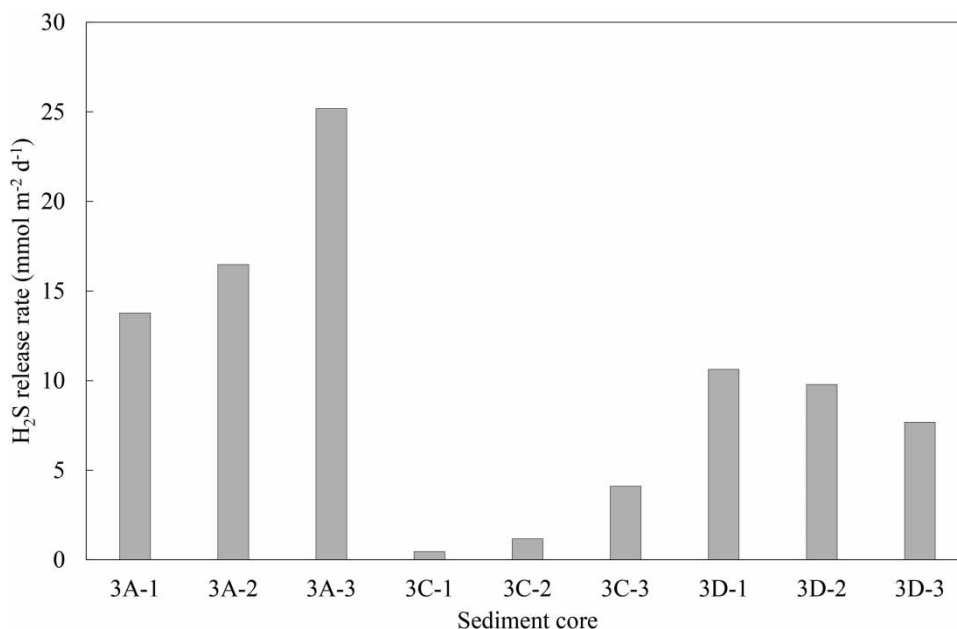
In contrast, 3C-1, 3C-2, and 3C-3 (FeOOH) showed almost no increase during the first 2 d. This reflected the complete suppression of  $\text{H}_2\text{S}$  release and stood in sharp contrast to the performance of  $\text{Fe}_2\text{O}_3$ , while being qualitatively consistent with Experiment 1. This suggests that the chemical form of the iron material used is a particularly important factor that influences its reactivity with  $\text{H}_2\text{S}$ . This finding is consistent with that of Sun *et al.* (2019) and indicates that FeOOH exhibits a larger specific surface area and higher reactivity to sulfide than  $\text{Fe}_2\text{O}_3$ .

$\text{H}_2\text{S}$  release was completely suppressed by FeOOH for 5 d in Experiment 1, whereas it was observed for only 2 d in Experiment 3. This may be caused by a larger  $\text{H}_2\text{S}$  release potential in the latter experiment ( $18.5 \text{ mmol m}^{-2} \text{ d}^{-1}$  on average in the reference cores) than in the former ( $10.2 \text{ mmol m}^{-2} \text{ d}^{-1}$  on average in the reference cores) (see the ' *$\text{H}_2\text{S}$  trap rate by iron materials*' section). Indeed, the free sulfide content in the sediments in Experiment 3 ( $14.8\text{--}228 \text{ mg L}^{-1}$ ) was higher than that in Experiment 1 ( $0.62\text{--}136 \text{ mg L}^{-1}$ ). Another explanation could relate to the different iron materials used. Experiment 1 used residue obtained after boiling ferric chloride aqueous solution, whereas Experiment 3 used a commercially available FeOOH. In both cases, the subsequent increases in  $\text{H}_2\text{S}$  were much slower than those in the references, especially after 120 h (Figure 7), and the suppression effects of the  $\text{Fe}_2\text{O}_3$  and FeOOH treatments lasted for at least three weeks.

The  $\text{H}_2\text{S}$  release rates from 3A-1, 3A-2, and 3A-3 (reference) were higher than those in the previous two experiments and showed much wider variations under the same conditions ( $18.5 \pm 4.9 \text{ mmol m}^{-2} \text{ d}^{-1}$ ) (Figure 8). 3D-1, 3D-2, and 3D-3 ( $\text{Fe}_2\text{O}_3$ ) achieved  $\sim 50\%$  suppression on average ( $9.4 \pm 1.2 \text{ mmol m}^{-2} \text{ d}^{-1}$ ) relative to that observed in the references; this



**Figure 7** | Time series of  $\text{H}_2\text{S}$  concentration in the overlying water in Experiment 3.



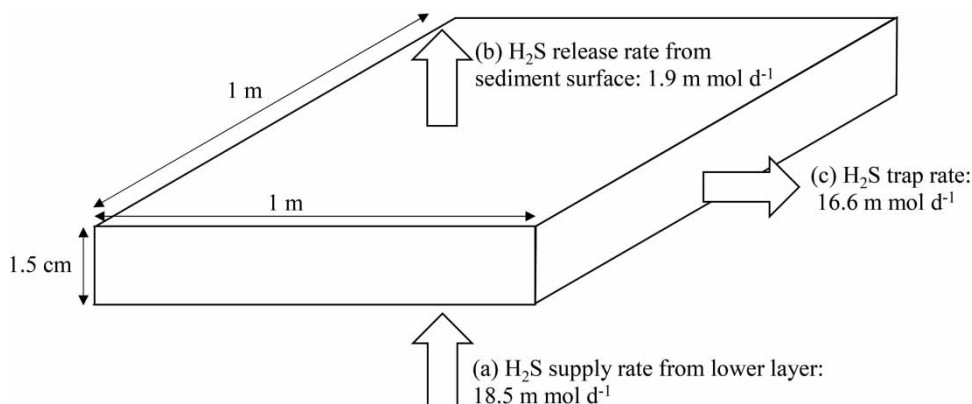
**Figure 8** | H<sub>2</sub>S release rates in Experiment 3.

was a weaker effect than that observed in Experiment 1 (97% suppression), in which similar amounts of the iron materials were added to the cores. FeOOH achieved ~90% suppression on average in Experiment 3 ( $1.9 \pm 1.6$  mmol m<sup>-2</sup> d<sup>-1</sup>), but not complete suppression (unlike in Experiment 1). This might have been caused by the difference in the free sulfide content of the tested sediment between the two experiments (see Supplementary Material, Tables S1 and S3).

## DISCUSSION

### H<sub>2</sub>S trap rate by iron materials

As the chemical analysis of the sediment pore water was conducted using samples that were 1.5 cm thick, the surface layer of sediment can be modeled as a rectangular box with a square base, sides of 1 m, and a height of 1.5 cm (Figure 9), to which sufficient FeOOH is supplied and in which no H<sub>2</sub>S is produced. Based on the average H<sub>2</sub>S release rate from the reference cores in Experiment 3, it can be assumed that H<sub>2</sub>S was supplied at 18.5 mmol d<sup>-1</sup> from below. Similarly, based on the average H<sub>2</sub>S release rates from the FeOOH-treated cores, it can be assumed that H<sub>2</sub>S was released at the rate of 1.9 mmol d<sup>-1</sup> from the surface. From the difference in these values, the trap rate of H<sub>2</sub>S by FeOOH in this box can be estimated as 16.6 mmol d<sup>-1</sup>.



**Figure 9** | Schematic diagram of H<sub>2</sub>S balance in the sediment surface layer.

However, the volume-specific  $H_2S$  trap rate in the surface layer ( $R_V$ ) is expressed by Fossing *et al.* (2004) as the product of the reaction rate constant,  $k$ , the  $H_2S$  concentration,  $C_{H_2S}^S$ , and the divalent iron concentration,  $C_{Fe^{2+}}^S$ , as given by Equation (2):

$$R_V = k C_{H_2S}^S C_{Fe^{2+}}^S \quad (2)$$

Fossing *et al.* (2004) reported a reaction rate,  $k$ , of  $650 \text{ m}^3 \text{ mol}^{-1} \text{ d}^{-1}$  ( $7.5 \times 10^{-7} \text{ L micromol}^{-1} \text{ s}^{-1}$ ; K13 in their study). Further, Poulton *et al.* (2002) concluded that the  $H_2S$  trap rate depends on the initial  $H_2S$  and divalent iron concentrations. Hence, they were set to 1.30 and  $0.0125 \text{ mmol L}^{-1}$ , respectively, in the present study; these were the initial concentrations of reference core, 3A-1. Based on these values, the  $H_2S$  trap rate in the theoretical box could be estimated as  $15.8 \text{ mmol d}^{-1}$ , which was very close to the estimated value ( $16.6 \text{ mmol d}^{-1}$ ) based on the  $H_2S$  release rate in Experiment 3. Therefore, we conclude that the  $H_2S$  suppression effect of FeOOH treatment was quantitatively confirmed by chemical kinetics.

The difference between the near-perfect suppression of  $H_2S$  release observed in Experiment 1 and the slightly worse performance in Experiment 3, despite the use of similar levels of FeOOH, may be due to the differences in the sedimentary free sulfide content between the two experiments (Supplementary Material, Tables S1 and S3). In the latter, the  $H_2S$  release rate ( $18.5 \text{ mmol d}^{-1}$ ) slightly exceeded the trap rate of  $H_2S$  by FeOOH ( $16.6 \text{ mmol d}^{-1}$ ), resulting in the release of some  $H_2S$  from the sediment ( $1.9 \text{ mmol d}^{-1}$ ). In contrast, the  $H_2S$  release of the reference cores in Experiment 1 was  $\sim 10.2 \text{ mmol d}^{-1}$ , which is less than the FeOOH trap rate, allowing the near-perfect suppression of  $H_2S$  release.

### Concentration of iron material required to trap $H_2S$

The ratio of the reaction rate of  $H_2S$  and divalent iron to the supply of  $H_2S$  (i.e., the supply from below the sediment layer) decides the  $H_2S$  trap rate. Therefore, we conducted a rough estimation of the iron concentration threshold that would prevent  $H_2S$  release from sediments. Assuming a constant  $H_2S$  concentration in the bulk region of deeper sediments, a linear profile of  $H_2S$  concentration in the surface layer, and the absence of  $H_2S$  in the overlying water (Figure 10), the diffusive flux of  $H_2S$  ( $F$ )

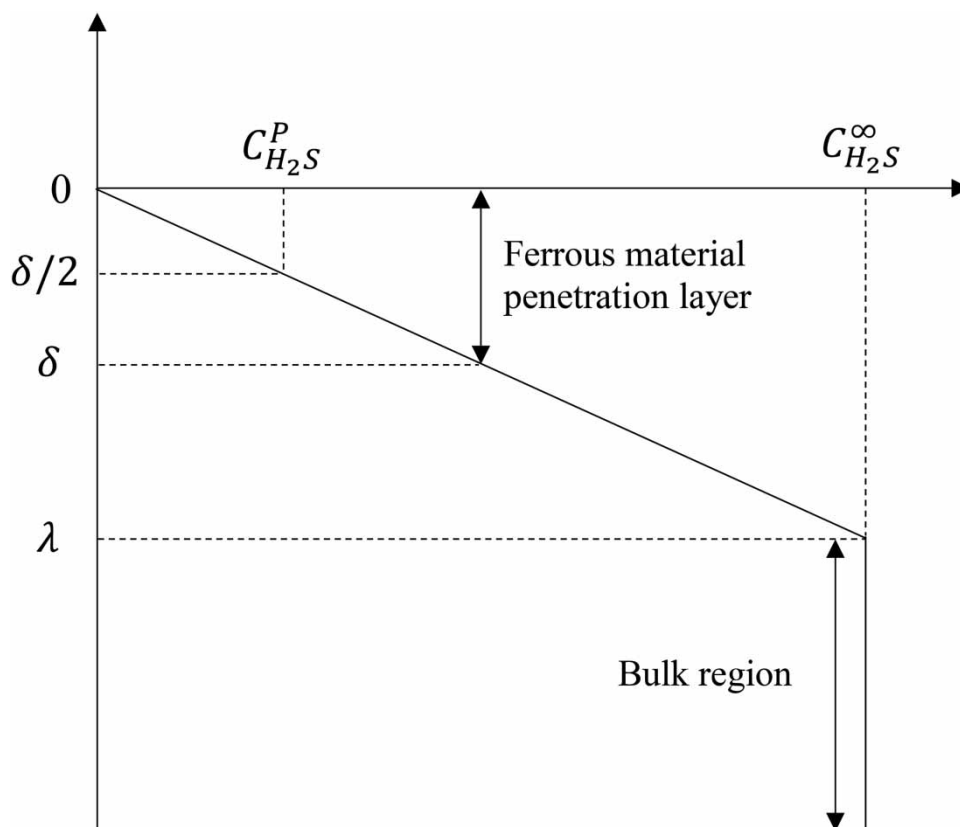


Figure 10 | Schematic view of  $H_2S$  profile.

can be approximately expressed as:

$$F = D \frac{C_{H_2S}^{\infty}}{\lambda} \quad (3)$$

where  $D$  is the apparent diffusion coefficient of  $H_2S$  in pore water,  $C_{H_2S}^{\infty}$  is the  $H_2S$  concentration in the bulk region, and  $\lambda$  is the thickness of the sediment layer, in which  $H_2S$  concentration steadily increases with depth (Inoue & Nakamura 2012).

Moreover,  $\delta$  is defined as the penetration depth of iron treatment. As a prerequisite for the following discussion,  $\delta$  should be smaller than  $\lambda$ .  $C_{H_2S}^P$  is also defined as the average  $H_2S$  concentration in the layer penetrated by iron material, which can have a linear profile and can thus be roughly expressed as:

$$C_{H_2S}^P = \frac{\delta}{2\lambda} C_{H_2S}^{\infty} \quad (4)$$

Referring to Equation (2), the area-specific  $H_2S$  trap rate in the iron penetrated layer ( $R_A$ ) is expressed by the product of the reaction rate constant  $k$ , the  $H_2S$  and divalent iron concentrations as representative values in the layer ( $C_{H_2S}^P$  and  $C_{Fe^{2+}}^P$ , respectively), and the penetration depth of the iron treatment  $\delta$ :

$$R_A = k C_{H_2S}^P C_{Fe^{2+}}^P \delta = \frac{k\delta^2}{2\lambda} C_{H_2S}^{\infty} C_{Fe^{2+}}^P \quad (5)$$

To suppress  $H_2S$  release,  $R_A$  must exceed  $F$ , suggesting the following simple conditional criterion:

$$C_{Fe^{2+}}^P > \frac{2D}{k\delta^2} \quad (6)$$

Practically,  $C_{Fe^{2+}}^P$  is controlled by the dynamic equilibrium of the diffusive supply of  $H_2S$  and the  $H_2S$  trap rate; its value should exceed the criterion defined in Equation (6) to suppress  $H_2S$  release from the sediments. In addition, the area-specific amount of divalent iron  $M$  should satisfy the following criterion:

$$M = C_{Fe^{2+}}^P \delta > \frac{2D}{k\delta} \quad (7)$$

This reveals that the required amount of iron material is inversely proportional to  $\delta$ . As the reaction rate constant  $k$  and apparent diffusion coefficient  $D$  are invariable physical properties, the penetration depth  $\delta$  can be considered one of the most important parameters that determines the level of iron material application.

### Temporal persistence of the suppression effect

We set the maximum experimental period to three weeks throughout this study to avoid influences on the  $H_2S$  release rate from changes in sediment quality. However, as this period was too short to directly assess the *in situ* persistence of suppression from iron material treatment, we attempted to estimate it instead. Kleeberg *et al.* (2013) applied 500 g  $m^{-2}$  iron to a dimictic lake and confirmed a long-term effect. In Experiments 1 and 3, 38.5–85.5 mmol iron material was applied to cylindrical cores with an internal diameter of 10 cm, which was equivalent to 274–608 g  $m^{-2}$  (Table 1). As these values represent the same order of magnitude as Kleeberg's application, a substantial long-term effect could be expected for our methods as well.

For example, 63.0 mmol of iron material added to a core from Experiment 3 would equal 8.02 mol  $m^{-2}$ . Assuming that equimolar amounts of  $H_2S$  and iron combine, 8.02 mol  $m^{-2}$  of treatment would be equivalent to an  $H_2S$  release of 18.5 mmol  $m^{-2} d^{-1}$  for ~434 d. This would also be equivalent to a release of 5.0 mmol  $m^{-2} d^{-1}$  for ~1,600 d in Experiment 2. Therefore, we suggest that the level of iron material treatment used in this study was roughly capable of suppressing  $H_2S$  release for more than a year.

## Application In the field

Slag has been widely applied to environments to induce positive effects, such as creating reef-like habitats (Chou *et al.* 2002). However, it also has some limitations, including the release of heavy metals, increases in the local pH, and the requirement of more than a 10 cm of slag (thickness) to suppress H<sub>2</sub>S release from sediments (Miyata *et al.* 2014). These disadvantages may be negligible in open and water-exchangeable areas. However, in more enclosed areas, such as dredged harbors and navigation channels, water exchange is not expected to occur and such disadvantages can manifest. Moreover, dredging is frequently conducted in such areas to maintain their navigability. However, applying slag to a navigation channel would increase the frequency of dredging required; therefore, its application in a navigation channel should be avoided.

## CONCLUSIONS

All iron material treatments exhibited some suppression effects, with FeOOH being most effective. Pure iron had a high reduction potential that negatively affected the ORP of the sediment, while FeOOH exhibited an oxidation potential that increased the ORP. Treating sediment surfaces with ~10 mol of iron material per square meter could suppress H<sub>2</sub>S release from sediments for at least three weeks.

This suppression depends on the relationship between the diffusive H<sub>2</sub>S supply from bottom of the sediment and the H<sub>2</sub>S trap rate owing to the iron treatment. A simplified model suggested that the minimum concentration of iron material required could be determined from the diffusivity of H<sub>2</sub>S, the reaction rate constant of the reaction between H<sub>2</sub>S and the iron material, and the treatment penetration depth. As the former two are invariable physical properties, the penetration depth is therefore the primary parameter controlling the H<sub>2</sub>S release rate. We theoretically estimated that treatment with 8 mol m<sup>-2</sup> of iron material could therefore suppress H<sub>2</sub>S release for over a year.

The three types of iron material investigated offer alternatives to the traditional but problematic use of slag from steelmaking, while contributing to the more effective utilization of iron materials for H<sub>2</sub>S suppression in urban rivers, lakes, aquaculture ponds, and coastal areas in the future. However, the potential harmful effects on aquatic organisms have not yet been considered and this will be the focus of subsequent research.

To summarize, it is important for researchers and decisionmakers to have several options, and they should select the most suitable measures depending on the environmental circumstances. Therefore, the application of the iron materials used in this study (Fe, Fe<sub>2</sub>O<sub>3</sub>, and FeOOH) is an alternative and promising measure for areas in which slag application is unfavorable.

## ACKNOWLEDGEMENTS

This study was partly supported by the Port and Airport Departments of the Chubu Regional Bureau, Ministry of Land, Infrastructure, Transport and Tourism, Japan. The authors are grateful to the staff of Aichi Fisheries Research Institute for their technical help.

## DATA AVAILABILITY STATEMENT

Data cannot be made publicly available; readers should contact the corresponding author for details.

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First received 15 October 2021; accepted in revised form 1 November 2021. Available online 12 November 2021