

Remediation of Coastal Marine Sediment using Iron

Ahmad Seiar Y.^{1,*}, Y. Nakamura¹, T. Miyatuji¹, Y. Hagino², T. Kobayashi²,
Y. Shigeoka² and T. Inoue³

¹Institute of Urban Innovation, Yokohama National University, 79-5 Tokiwadai, Hodogaya-ku, Yokohama, Japan

²Tokyo Kyuei Co. Ltd. 3-1-15 Nihonbashi, Chuoh-ku, Tokyo, Japan

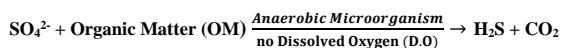
³Environment Information Research Group, Port and Airport Research Institute, 3-1-1 Nagase, Yokosuka, Japan

Keywords: Sedimentary Sulfide-release, Iron, Iron Hydroxide, Anoxia, Laboratory Experiment.

Abstract: Laboratory experiments were conducted to evaluate the effectiveness of iron application to surface sediment on the suppression of hydrogen sulfide release from sediments. By using sediments cores collected from Mikawa Bay, Japan at every month from June to September 2017, incubation experiments were made for three weeks under anoxic conditions with or without application of the iron containing compounds; the iron oxide or iron hydroxide. The results revealed that both uses of the iron oxide and iron hydroxide significantly reduced sulfide release flux from the sediment into the overlying water. Iron hydroxide was more effective than iron oxide in the suppression of sulfide release, as concluded from 21 day of incubation. While, no significant difference was observed among the control group after 21 day incubation. Therefore, it can be concluded that the application of iron to the sediment is a promising method to remediate contaminated sediments in eutrophic water body.

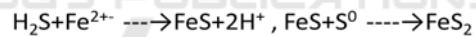
1 INTRODUCTION

Sediment is the important habitat for organisms living in the surface and into the bottom ground. It acts as the storehouse of nutrients in aquatic ecosystems. Eutrophication because of excess amount of nutrients supply to a water body causes high productivity that results in large amount of organic matters settle to the sediments. As the excess organic material is left to be decomposed, and if the amount of oxygen is insufficient, decomposition processes continue due to bacterial activities employing electron acceptors other than oxygen, this results in the reduction of sulfate, (Wang and Chapman, 1999; Levin et al., 2009; 2002; Yakushev et al., 2007; Ueda, 2013), as per equation,



In the absence of dissolved oxygen (DO) and in the presence of soluble Biological Oxygen Demand (BOD), *Desulfovibrio desulfuricans* (SRB) and other sulfate-reducing bacteria (SRB's) convert the sulfate ion to sulfide, which is highly toxic and fatal to benthic organisms. However, the irons have capacity to regulate the formation of sulfide by poisoning the

redox sequence and to form insoluble iron sulfide and pyrite compounds. The chemical equation showing this process is



keeping these points in view, for marine environmental remediation, we aim to propose a method for improving the sediment environment and conduct an elution experiment using an undisturbed sediment core added with various iron materials in laboratory experiments to precipitate hydrogen sulfide over a long period of time.

2 MATERIALS AND METHODS

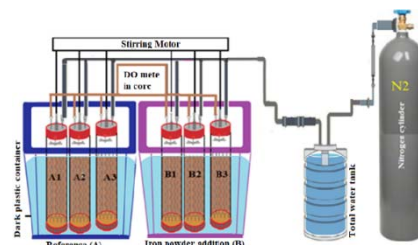


Figure 1: A schematic view of the experimental apparatus.

* http://www.cvg.ynu.ac.jp/G2/member_e.html

2.1 Sampling Locations

Intact sediment cores were taken from a fix point in the innermost part of Mikawa Bay, Japan, in order to evaluate the suppression effects of iron application to surface sediment on sulfide release rates. Mikawa Bay is a eutrophic coastal embayment's in which seasonal density stratification and associated hypoxic condition in the bottom water develop, in general, from June to September. In this study, sediment core samples were collected with acrylic pipe whose inner diameter of 10 cm and length of 50 cm, every month from June to September 2017. Temperature, salinity, DO, and turbidity were measured at every sampling occasions. All sampled sediment cores were immediately transferred to a laboratory to conduct sulfide release experiments with or without iron application to the surface sediment.

2.2 Laboratory Experiments

Total 6 (for experiments in June, July and August) or 9 (September) core samples were selected for incubation experiment. In the laboratory, the overlying water of each core was replaced with deoxygenated filtered seawater. For iron application cores, predetermined amount of iron compounds were applied to the surface of the sediment. Cores were then sealed by a top cap to keep anoxic condition during the course of the incubation period. DO meter to check anoxic condition and a stirrer to circulate the overlying water were also installed to a lid of pipe for each core. Cores were then incubated into a container keeping the same temperature of each the in-situ conditions. Bottom water temperature for June, July, August, and September experiments were 20.3, 21.7, 25.7 and 24.0 degree in Celsius, respectively.

The experiment was conducted with total four kind of treatments (Reference core A, core B with iron oxide applied to the surface, Unused core C, and core D added with iron hydroxide, which was performed only in September). In addition, each experimental treatment was performed in triplicate except the treatment B in June. Table 1 shows the amount of iron compounds applied for each experiment. Note that 5 g of iron oxide and 5.6 g of iron hydroxide are equivalent to the same Fe amount of 3.5 g.

The incubation experiments continued for three weeks. Water samples were collected to measure the dissolved sulfide and dissolved iron concentrations in the overlying water at appropriate time intervals during the incubation.

Table 1: List of treatments of the release experiment.

Treatments	Iron compounds	Amount of iron compounds applied [g]			
		June	July	Aug.	Sept.
A: Control	Reference-1	0	0	0	0
	Reference-2	0	0	0	0
	Reference-3	0	0	0	0
B: Iron oxide addition	Fe ₂ O ₃ -1	0.41	5	5	5
	Fe ₂ O ₃ -2	0.85	5	5	5
	Fe ₂ O ₃ -3	1.61	5	5	5
C: Experiment unused	Only use in chemical analysis and preparative				
D: Iron hydroxide addition	Fe(OH) ₃ -1	-	-	-	5.6
	Fe(OH) ₃ -2	-	-	-	5.6
	Fe(OH) ₃ -3	-	-	-	5.6

2.3 Chemical Analysis

Dissolved sulfide was analysed by the methylene blue method. In this method, a sulfide colouring reagent comprising iron chloride III (FeCl₃·6H₂O) and N, N-dimethyl-p-phenylenediamine sulphate dissolved in 6 M HCl solution were added into the sample for analysis. The absorbance of the solution was measured with a spectrophotometer at a wavelength of 667 nm. Dissolved divalent iron concentration was also analysed by the phenanthroline method.

Sediment quality was analysed after completion of the experiment. Sediments were sliced to 1.5 cm intervals, and water content, loss in ignition, TOC, COD, sulfide, TN, TP, T-Fe, and T-Mn were analysed for each sediment samples. Sediment pore water was obtained by squeezing over a 0.45 µm filter, then dissolved-sulfide concentrations were measured in pore waters. A part of the collected sediment samples was also used to analyze the hydrogen ion concentration index (pH), oxidation-reduction potential.

The data were analyzed using one-way analysis of variance (ANOVA) at 0.05% level of significance with the SPSS package (version 23 IBM).

3 RESULTS AND DISCUSSIONS

3.1 Dissolved Sulfide Concentration in the Overlying Water

Temporal changes of dissolved sulfide concentrations in the overlying water in each treatment are shown in Figure. 2 (a), (b), (c), and (d) for the experiments

conducted in June, July, August and September, respectively. For every cases, the concentration of dissolved sulfide in the overlying water monotonically increased related to sediment remediation in all the cores.

Result for the experiments in June shows relatively lower release of the dissolved sulfide into the overlying water even in the control cases (A1, A2, and A3). Order of the final concentration of dissolved sulfide for B-1, B-2, and B-3 did not follow the application amount of iron. Additionally, the final concentration for cases of the application of iron (Group B) showed no statistically significant difference from the control case (Group A). Therefore, for later experiments we used larger amount of iron compounds for triplicate sediment cores.

Table 2: Analysis of variance for reading comprehension of the studied variables in the sediment.

Parameter	Periods	F Value	P Value	Result
Dissolved sulfide concentrations in the overlying water	June	3.845	0.568	The result is not significant at $p < .05$.
	July and August	6.643	0.011	The result is significant at $p < .05$.
	September	8.924	0.000	The result is significant at $p < .01$.
Dissolved sulfide increase rate ($\text{mg}/\text{m}^2/\text{day}$)	June	0.064	0.804	The result is not significant at $p < .05$.
	July	0.891	0.367	The result is not significant at $p < .05$.
	August	5.515	0.407	The result is significant at $p < .05$.
	September	9.401	0.002	The result is significant at $p < .01$.

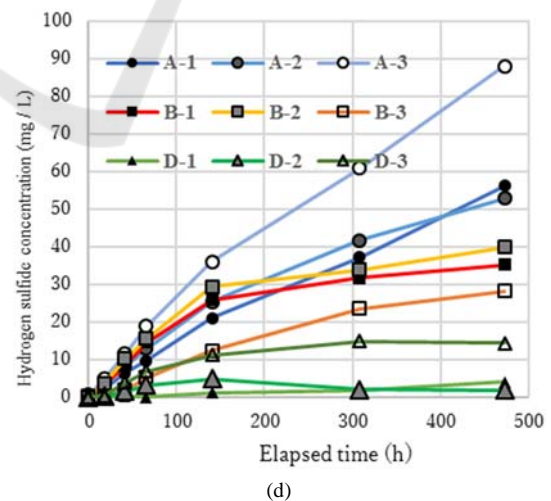
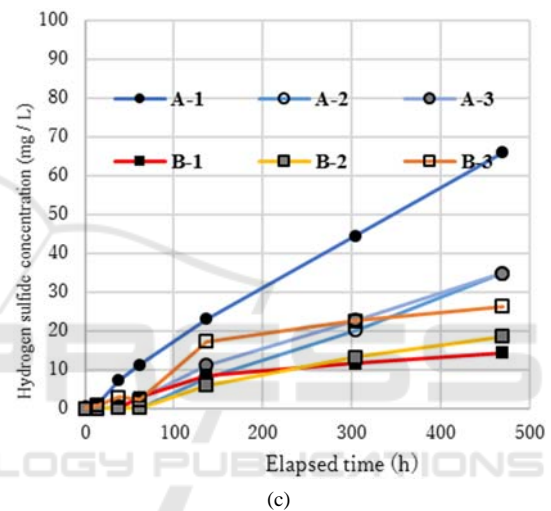
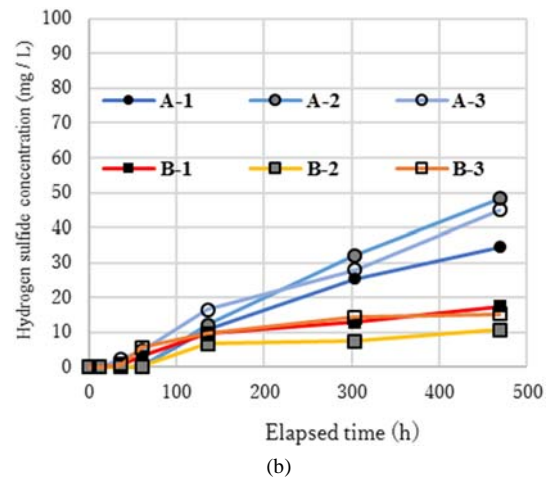
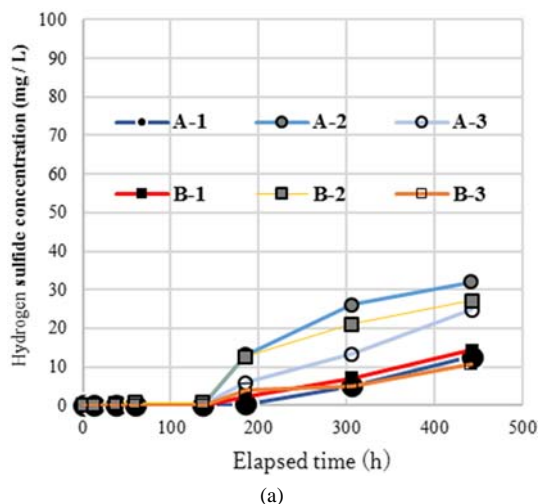


Figure 2: Temporal changes in dissolved sulfide concentration in the overlying water for (a) June, (b) July, (c) August, and (d) September experiments.

Results obtained from cores for July, August and September show a significant difference ($p < 0.05$) between the two treatment groups. Based on data obtained in July, for example, the final concentration of dissolved sulfide in the control cores (A-2, A-3, A-1) were 44.4, 40.6, and 31.9 mg/L, respectively. Whereas the final concentrations in the iron treatments core (B-2, B-3, B-1) indicated 9.4, 12.5, and 14.6 mg/L, respectively. These results showed remarkably lower values compared to the control cases as shown Figure 2 (b). The same tendency was observed for the third August experiments.

In the last experiment in September, iron hydroxide was also added to treatment groups. The final concentration of dissolved sulfide in the overlying water for iron hydroxide core (D-2, D-1, D-3) indicates 0.4, 3.8, and 10.7 mg/L, respectively, as shown in Figure 2 (d). These values were much smaller than iron oxide application core (B-3, B-1, B-2), in which those values were 23.2, 25.2, and 29.5 mg/L. The dissolved sulfide concentrations were quite high in the control core (A-3, A-1, A-2) with values of 73.6, 49.6, and 43.4 mg/L, respectively. Although the averaged final concentration was highest in the control case (A) in September, it was lowest in the iron hydroxide application (D). This suggests the relatively higher effectiveness of the iron hydroxide for the suppression of sulfide release. The lag time to appear significant increase in 5 mm dissolved sulfide concentration was longest in June. More than five days were necessary even in the control case. The lag time became gradually shorter in the later experiments. Especially in September, no apparent lag time was observed.

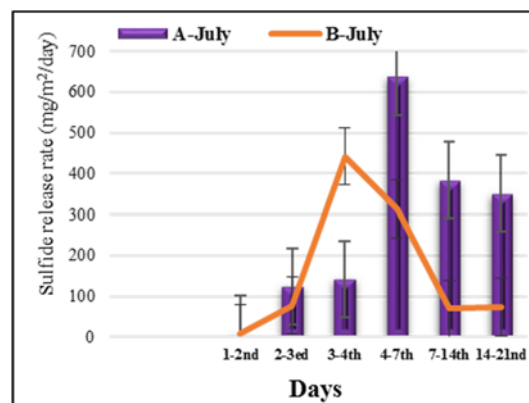
3.2 Dissolved Sulfide Release Rate

One of the practically important parameters is the release rate of dissolved sulfide from the sediment under anoxic conditions. Averaged release rates calculated for each time interval of the experiments are shown in Figure 3(a), (b), and (c), for July, August, and September experiments.

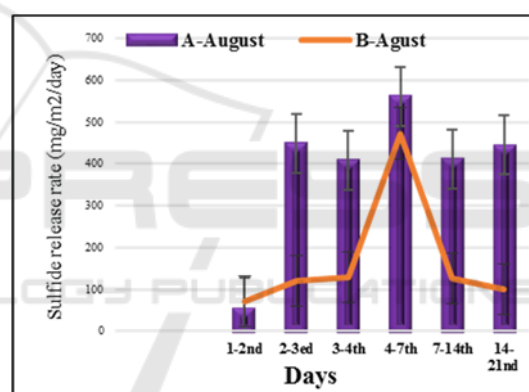
In July and August experiments, the release rate of dissolved sulfide in the control cores (A-1, A-2, A-3) in turn ranged from 2 to 556 mg/m²/day and 8 to 637 “mg m² d⁻¹”. However, in the experiment with iron material added, it ranged from 1 to 521 mg/m²/day and 8 to 422 mg/m²/day.

Results of September experiment demonstrated that the release rate as well as dissolved sulfide concentrations in the overlying water were significantly low with iron hydroxide core (D-2, D-1, D-3) ranging from 1 to 269 mg/m²/day. As shown in

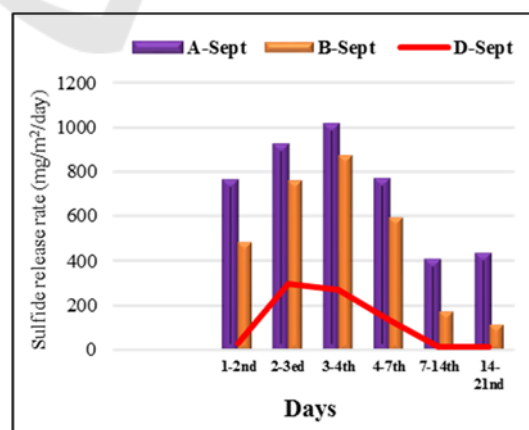
Figure 3(c), the second lowest value of the release rate of dissolved sulfide were obtained from core (B-3, B-1, B-2) were 116 to 845 mg/m²/day, respectively. The release rate were quite high in the control core (A-3, A-1, A-2) with values ranged from 409 to 1,014 mg/m²/day.



(a)



(b)



(c)

Figure 3: Release rate of dissolved sulfide for (a) July, (b) August, and (c) September experiments.

3.3 Sulfide Release Rate and Iron Concentration

Figure 4 shows comparison between sulfide release rates and divalent iron concentrations for July, August and September experiments. The divalent iron can react with dissolved sulfide to form particulate iron sulfide, which will precipitate to the sediment. Such reaction may under-estimate the release rates of dissolved sulfide. However, the concentration range of divalent iron is relatively low in these experiments.

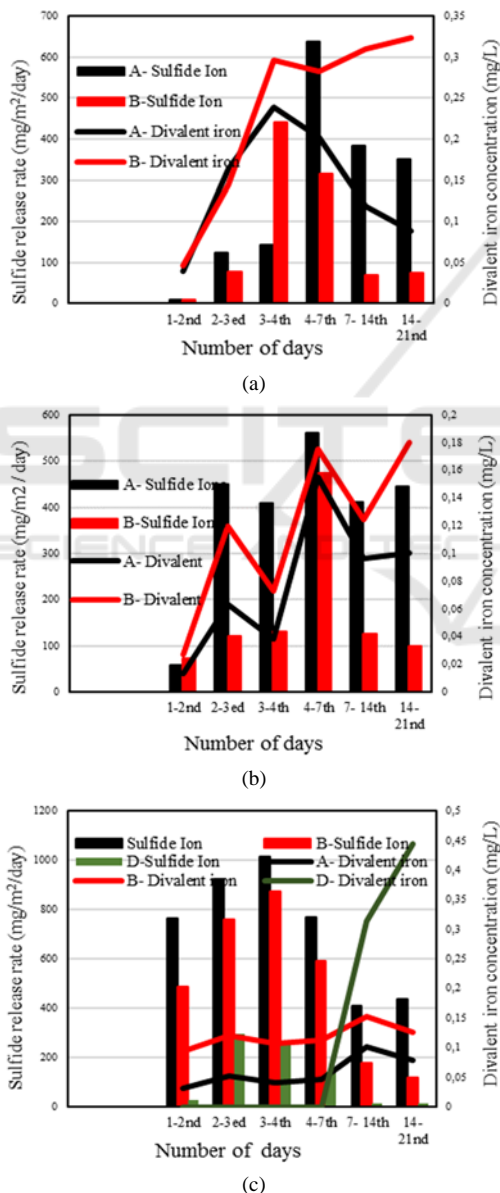


Figure 4: Comparison of sulfide release rates and divalent iron concentrations for (a) July, (b) August, and (c) September experiments.

Further quantitative analysis on this point would be necessary for further arguments.

4 CONCLUSIONS

The results revealed that both uses of the iron and iron-hydroxide significantly reduced sulfide release flux from the sediment into the overlying water. After the 21 days incubation, the average dissolved sulfides concentration in the overlying water of treatment group was significantly decrease ($p = .0001$). No significant difference was observed between the control group after 21 day incubation. Therefore, the application of iron to the sediment is a promising method to remediate contaminated sediments in eutrophic water body.

REFERENCES

- Ueda, K., 2013. Modeling of dissolved oxygen concentration recovery in water bodies and application to hypoxic water bodies. *World Envi.*, vol. 3, no. 2, pp. 52-59.
- Levin, L. A., Ekau, W., Gooday, A. J., Jorissen, F., Middelburg, J. J., Naqvi, W., Neira, C., Rabalais, N. N., and Zhang, J., 2009. Effects of natural and human-induced hypoxia on coastal benthos. *Biogeosciences Discuss.*, vol. 6, pp. 3563–3654.
- Yakushev, E. V., Pollehne, F., Jost, G., Kuznetsov, I., Schneider, B., and Umlauf, L., 2007. Analysis of the water column oxic/anoxic interface in the Black and Baltic seas with a numerical model. *Marine Chemistry*, vol. 107, pp. 388–410.
- Wang, F. and Chapman, P. M., 1999. Biological Implications of Sulfide in Sediment – A Review Focusing on Sediment Toxicity, *Environ Toxicol Chem.*, vol. 18, no. 11, pp. 2526-2532.