

## Supplementary Material

Aqueous mercury removal with carbonaceous and iron sulfide sorbents and their applicability as thin-layer caps in mercury-contaminated estuary sediment

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## 1. Characterization of physicochemical properties of sediment

### 1.1. Water content

The water content of air-dried sediment was measured by the weight method based on the Taiwan Environmental Protection Administration (TEPA) standard method (NIEA S280.62C). First, an empty 25 mL beaker was weighted ( $w_0$ ). Then, the beaker containing approximately 20 g of air-dried sediment ( $w_1$ ) was weighted. Afterward, the beaker with air-dried sediment was placed in an oven at 105°C for 24 h to remove the water ( $w_2$ ). Then, the weight of the oven-dried sediment with the beaker was recorded. The calculation of water content of the sediment is expressed as below:

$$\theta = \frac{w_1 - w_2}{w_2 - w_0} \times 100\% \quad (1)$$

### 1.2. pH value

Sediment pH value was measured by pH meter (Suntex SP-2300) based on TPEA standard method (NIEA S410.62C). The sample was prepared by mixing 20 g of dried sediment with 20 mL distilled water in a 100 mL beaker and stand for one hour to reach equilibrium. The pH value of the slurry was then measured.

### 1.3. Soil texture

For determination of soil texture, the sediment was measured by using the Bouyoucos hydrometer method [32]. Dried sediment of 50 g was placed into 600 mL beaker, 200 mL of DI water was added into and the mixture was stirred. After waiting for 20 minutes, the mixture was put into a blender metal container, 10 mL of 5% sodium metaphosphate solution was added and stirred with a blender. After that, the mixture was put into a 1000 mL graduated cylinder, a hydrometer was placed to the volumetric flask and stood for 40 seconds. The value of the hydrometer was recorded, designated as  $P_s$ . After 2 h, the reading of hydrometer was recorded, designated as  $P_c$ .

$$\text{Sand}(\%) = 100 - \frac{P_s}{W_s} \times 100 \quad (2)$$

$$\text{Clay}(\%) = 100 - \frac{P_c}{W_s} \times 100 \quad (3)$$

$$\text{Silt}(\%) = 100 - [\text{sand}(\%) + \text{clay}(\%)] \quad (4)$$

### 1.4. Organic carbon

Sediment organic carbon content was measured by Walkley-Black wet oxidation [33]. Dried sediment (100 mesh) of 0.5 g was placed into a 500 mL Erlenmeyer flask, 10 mL of 1 N potassium dichromate solution was added and mixed well. Then, 20 mL of sulfuric acid was added, the flask was swirled rapidly and stood for 30 min. Afterward, 200 mL of water, 10 mL of phosphorus acid and 30 drops of diphenylamine indicator were added to the flask, and the solution was titrated with 0.5 N ammonium

iron sulfate solution till the solution turned to dark green, which represented the titration endpoint was reached. The organic carbon content of sediment was calculated by the following equation:

$$\text{organic carbon content(g/kg)} = V \times \left(1 - \frac{V_s}{V_b}\right) \times \frac{12}{4 \times 1000} \times 1.3 \times \frac{1000}{\text{dried soil(g)}} \quad (5)$$

where V (mL) is the volume of 1 N potassium dichromate solution,  $V_s$  (mL) is the volume of  $\text{Fe}^{2+}$  for sample titration and  $V_b$  (mL) is the volume of  $\text{Fe}^{2+}$  in blank titration.

### 1.5. Cation exchange capacity (CEC)

The sediment cation exchange capacity was measured by the ammonium acetate method based on the TEPA standard method (NIEA S201.61C); dried sediment of 5 g was placed in a column, 100 ml of 1 M ammonium acetate ( $\text{NH}_4\text{COOH}$ ) was added into a separatory funnel, which was then turned on to leach the sediment. Before adding 100 mL of 10% acidic sodium chloride ( $\text{NaCl}$ ) to the separatory funnel, 100 mL of ethanol was added to the separatory funnel to leach the excess  $\text{NH}_4\text{COOH}$  solution. The leach liquor of acidic  $\text{NaCl}$  solution was collected which contains  $\text{NH}_4^+$  as  $\text{Na}^+$  displaces it on the cation absorption site of the sediment. Using the Kjeldahl's distillation method, 5 ml 10 N sodium hydroxide ( $\text{NaOH}$ ) solution was added to 10 mL of the previous leach liquor. Erlenmeyer flask with 10 mL boric acid indicator was placed as a clue to collect the distillate. Then, the flask was took off the apparatus, let it cool down. After that, followed by titration of distillate with 0.01 N hydrochloric acid ( $\text{HCl}$ ) until the color of indicator change to original color and record the titrate volume, CEC of sediment can be calculated by the following equation:

$$\text{CEC (cmol(+) / kg sediment)} = N \times \frac{S-B}{A} \times \frac{100}{\text{dried sediment (g)}} \times 100 \quad (6)$$

where N is the concentration of  $\text{HCl}$ , S (V) is the volume of titration for sediment sample, B (V) is the volume of titration for blank, A (V) is the draw out the volume of distillate.

**Table S1.** Freshwater and seawater ion species concentration

Ion	Freshwater (g/kg)	Seawater (g/kg)
Na <sup>+</sup>	0.026	10.78
K <sup>+</sup>	0.002	0.386
Mg <sup>2+</sup>	0.025	1.295
Ca <sup>2+</sup>	0.016	0.414
Cl <sup>-</sup>	0.002	19.36
SO <sub>4</sub> <sup>2-</sup>	0.135	2.711
Br <sup>-</sup>	-	0.066
F <sup>-</sup>	-	0.001

**Table S2.** Hg(II) speciation at various salinity levels

Species	log K	Fraction (%)		
		Freshwater	Estuary water	Seawater
Hg(OH) <sub>2</sub>	-3.94	95.97	0.094	0.014
HgOHCO <sub>3</sub> <sup>-</sup>	11.39	1.241	-	-
HgCO <sub>3(aq)</sub>	18.29	0.244	-	-
HgCl <sub>2(aq)</sub>	20.19	0.013	11.08	3.964
HgCl <sub>3</sub> <sup>-1</sup>	21.19	-	30.22	21.77
HgCl <sub>4</sub> <sup>-2</sup>	21.79	-	53.99	72.89
HgClOH <sub>(aq)</sub>	10.44	2.527	2.326	0.544
HgBr <sub>2(aq)</sub>	24.29	-	0.291	0.116
HgBr <sub>3</sub> <sup>-1</sup>	26.67	-	0.029	0.024
HgBrCl <sub>(aq)</sub>	22.18	-	1.519	0.573
HgBrOH <sub>(aq)</sub>	12.40	-	0.454	0.112

**Table S3.** The partitioning coefficients for Hg adsorptions at various salinity levels

	K <sub>D</sub> (mg/g/μM)		
	Freshwater system	Estuary system	Seawater system
	Without DOM		
AC	0.66±0.21	1.89±1.07	1.43±0.40
SAC	1.52±0.04	1.75±0.51	2.01±1.16
FeS	2.64±0.91	4.16±4.15	4.29±2.20
	With DOM		
AC	0.29±0.42	1.19±1.02	1.24±0.09
SAC	0.86±0.08	2.36±0.61	1.58±0.21
FeS	0.86±0.10	5.26±2.17	3.44±1.53

**Table S4.** A one-way ANOVA or one-way ANOVA on ranks based on normality test, followed by a post hoc test ( $p < 0.05$ ) used to determine the significance differences among various sorbents.

Freshwater system

Sorbent	Temp (°C)	DO (mg/L)	pH	DOM (mg/L)	Fe (mg/L)	EC (uS/cm)	ORP (mV)	THg (ng/L)	MeHg (ng/L)
AC	24.6 ± 1.92 <sup>a</sup>	2.98 ± 0.38 <sup>a</sup>	7.81 ± 0.08 <sup>a</sup>	6.14 ± 4.63 <sup>a</sup>	0.041 ± 0.007 <sup>b</sup>	2416 ± 473 <sup>a</sup>	92.1 ± 26.9 <sup>a</sup>	164 ± 202 <sup>a</sup> 99.0 ± 58.7 <sup>a,*</sup>	0.249 ± 0.210 <sup>b</sup>
SAC	24.5 ± 2.09 <sup>a</sup>	2.73 ± 0.23 <sup>a</sup>	7.84 ± 0.10 <sup>a</sup>	7.62 ± 4.98 <sup>a</sup>	0.052 ± 0.021 <sup>bc</sup>	2511 ± 500 <sup>a</sup>	126 ± 37.7 <sup>a</sup>	122 ± 73.8 <sup>a</sup>	0.577 ± 0.362 <sup>b</sup>
FeS	24.3 ± 2.23 <sup>a</sup>	2.62 ± 0.44 <sup>a</sup>	7.81 ± 0.09 <sup>a</sup>	6.91 ± 2.77 <sup>a</sup>	0.224 ± 0.321 <sup>ac</sup>	2448 ± 464 <sup>a</sup>	93.5 ± 32.0 <sup>a</sup>	177 ± 139 <sup>a</sup> 137 ± 73.2 <sup>a,*</sup>	0.635 ± 0.520 <sup>b</sup>
Control	24.4 ± 2.12 <sup>a</sup>	2.79 ± 0.37 <sup>a</sup>	7.81 ± 0.06 <sup>a</sup>	10.4 ± 3.13 <sup>a</sup>	0.251 ± 0.097 <sup>a</sup>	2467 ± 451 <sup>a</sup>	91.4 ± 31.3 <sup>a</sup>	176 ± 85.2 <sup>a</sup>	6.09 ± 3.31 <sup>a</sup>

Estuary system

Sorbent	Temp (°C)	DO (mg/L)	pH	DOM (mg/L)	Fe (mg/L)	EC (uS/cm)	ORP (mV)	THg (ng/L)	MeHg (ng/L)
AC	24.4 ± 2.10 <sup>a</sup>	2.82 ± 0.46 <sup>a</sup>	7.75 ± 0.10 <sup>ab</sup>	3.84 ± 3.55 <sup>a</sup>	0.233 ± 0.035 <sup>b</sup>	38056 ± 525 <sup>a</sup>	121 ± 22.2 <sup>a</sup>	126 ± 72.9 <sup>a</sup>	0.247 ± 0.135 <sup>a</sup>
SAC	24.3 ± 2.19 <sup>a</sup>	2.79 ± 0.42 <sup>a</sup>	7.81 ± 0.07 <sup>b</sup>	4.88 ± 3.57 <sup>a</sup>	0.239 ± 0.054 <sup>b</sup>	38067 ± 829 <sup>a</sup>	119 ± 26.2 <sup>a</sup>	201 ± 348 <sup>a</sup> 85.2 ± 43.5 <sup>a,*</sup>	0.352 ± 0.298 <sup>a</sup>
FeS	24.4 ± 2.12 <sup>a</sup>	2.73 ± 0.40 <sup>a</sup>	7.72 ± 0.06 <sup>a</sup>	6.21 ± 2.80 <sup>a</sup>	0.333 ± 0.094 <sup>a</sup>	38000 ± 763 <sup>a</sup>	65.4 ± 46.0 <sup>b</sup>	114 ± 44.6 <sup>a</sup>	0.768 ± 0.866 <sup>a</sup>
Control	24.4 ± 2.15 <sup>a</sup>	2.67 ± 0.27 <sup>a</sup>	7.72 ± 0.06 <sup>a</sup>	6.64 ± 2.24 <sup>a</sup>	0.252 ± 0.048 <sup>ab</sup>	37767 ± 748 <sup>a</sup>	113 ± 20.1 <sup>a</sup>	143 ± 54.6 <sup>a</sup>	0.469 ± 0.274 <sup>a</sup>

Different letters for temperature, DO, pH, DOM, and Fe of microcosms and EC, ORP, THg, and MeHg of overlying water indicate a significant difference at  $p < 0.05$ . For example, the value with letter b are significantly different from that with letter a. The values with \* are the averaged THg concentrations excluding the extremely high value during the microcosm tests.



**Figure S1.** Photos of the microcosms on (a) day 25 as the capping materials were initially applied and (b) on day 65

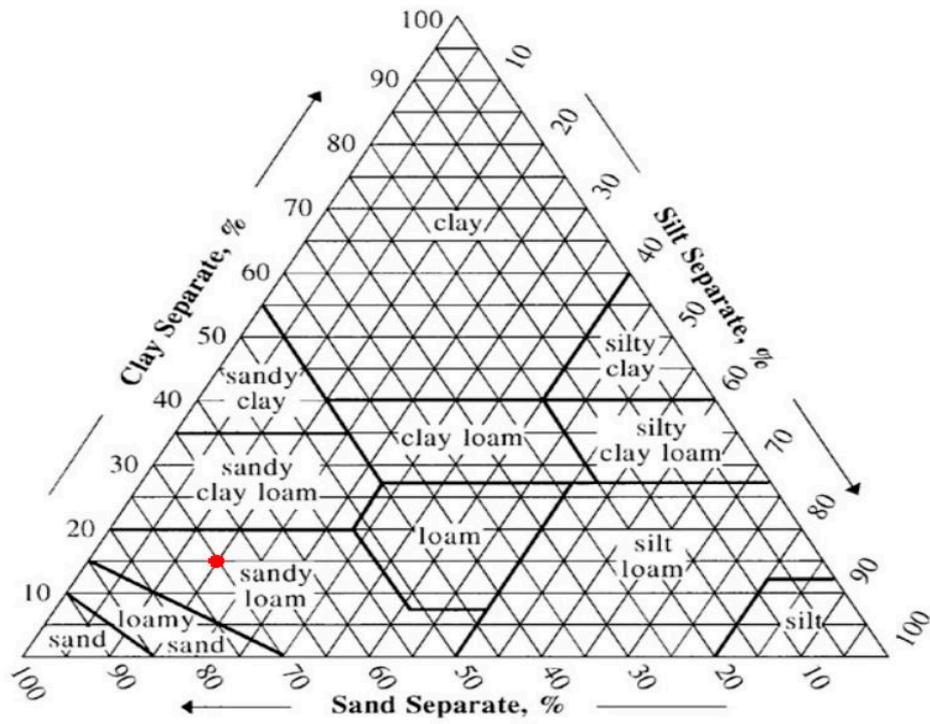


Figure S2. An-Shun site sediment texture

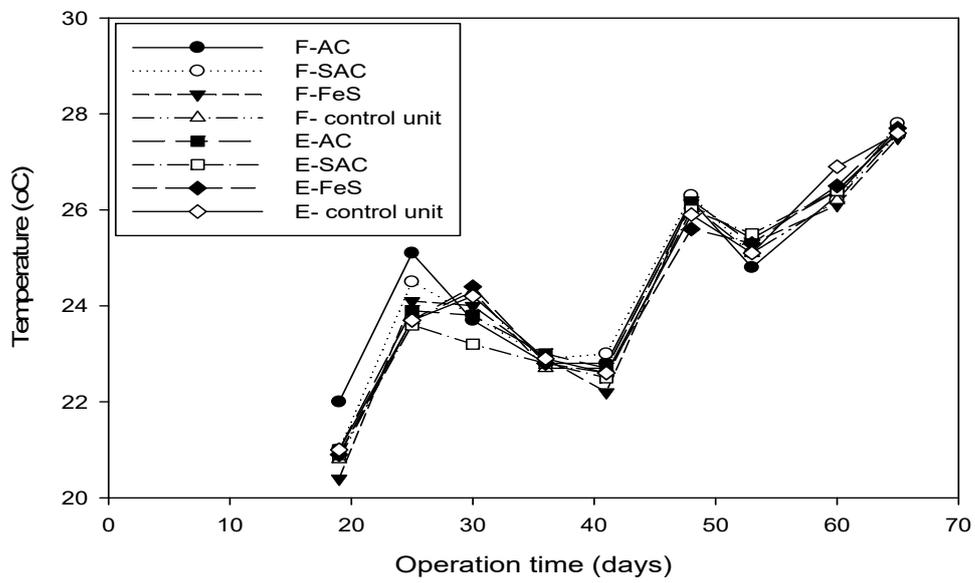
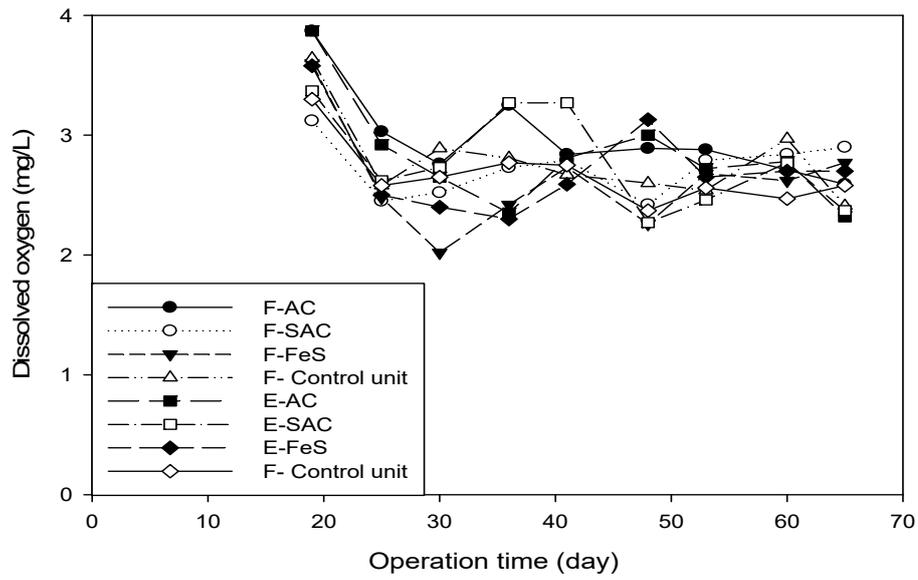
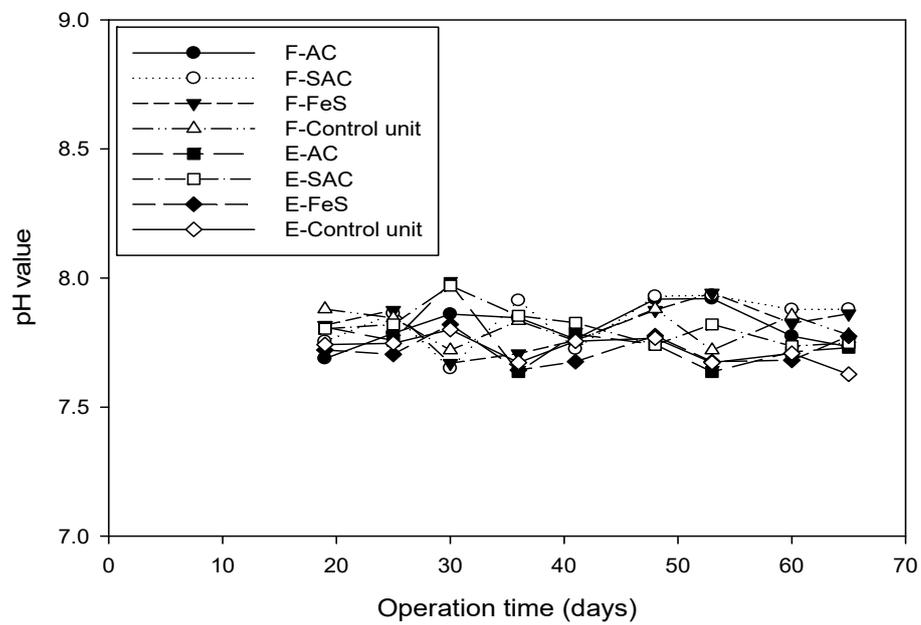


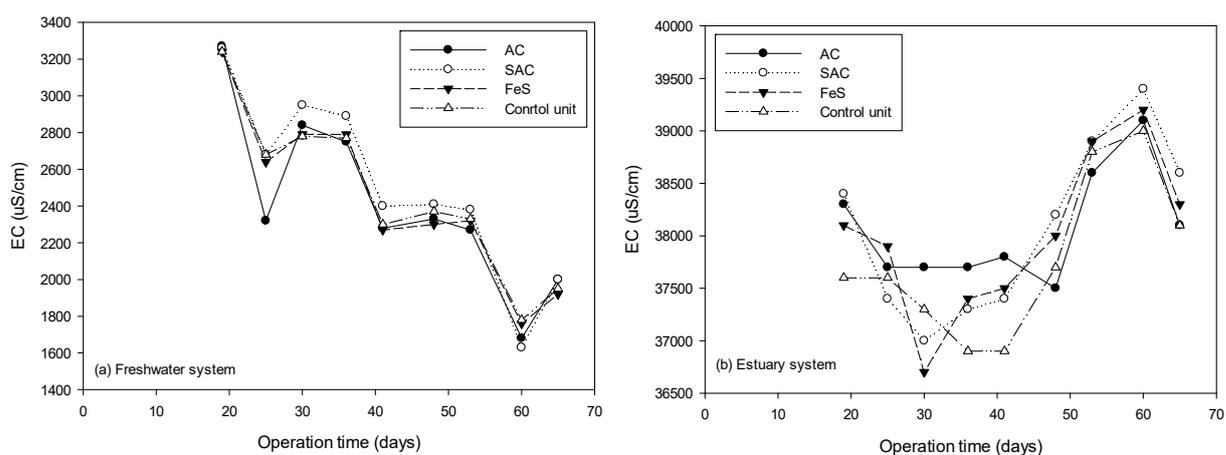
Figure S3. The temperature of microcosms (the symbol F refers to freshwater system and the symbol E refers to estuary system)



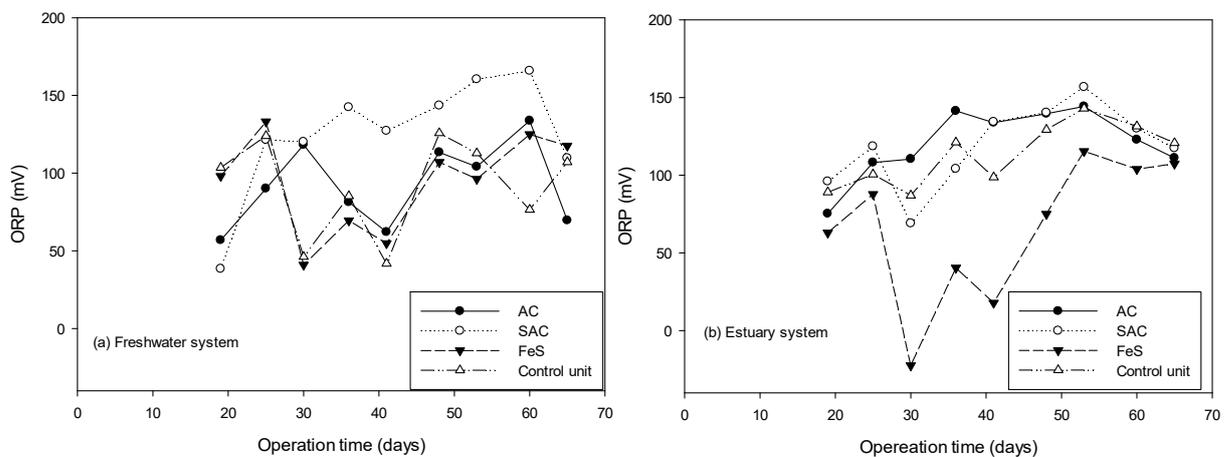
**Figure S4.** The dissolved oxygen for the microcosms (the symbol F refers to freshwater system and the symbol E refers to estuary system).



**Figure S5.** The pH value variation of microcosms (the symbol F refers to freshwater system and the symbol E refers to estuary system)



**Figure S6.** The electricity conductivity of overlying water in (a) freshwater system and (b) estuary system



**Figure S7.** The oxidation reduction potential of overlying water in (a) freshwater system and (b) estuary system.

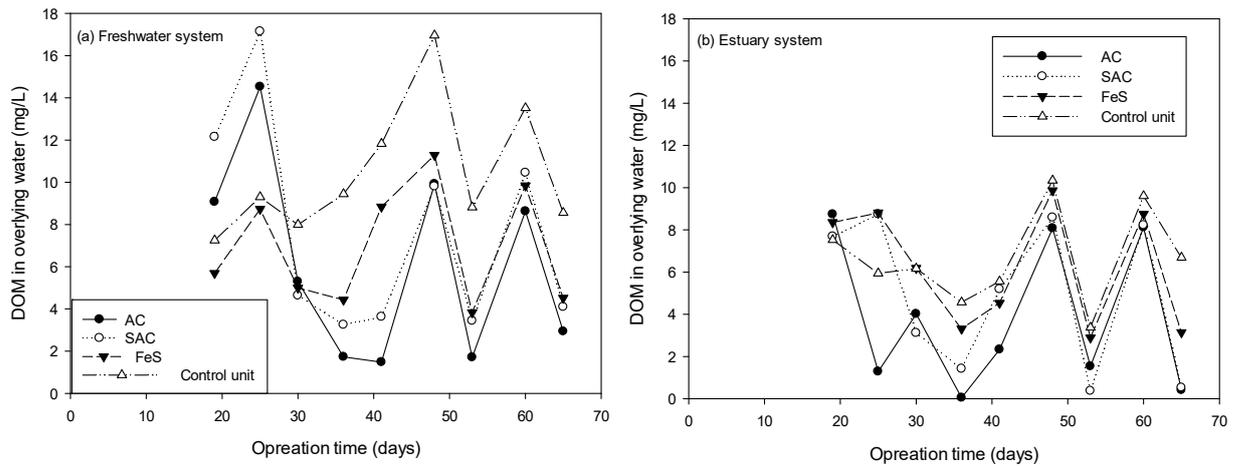


Figure S8. DOM variation of microcosms for (a) freshwater system; (b) estuary system

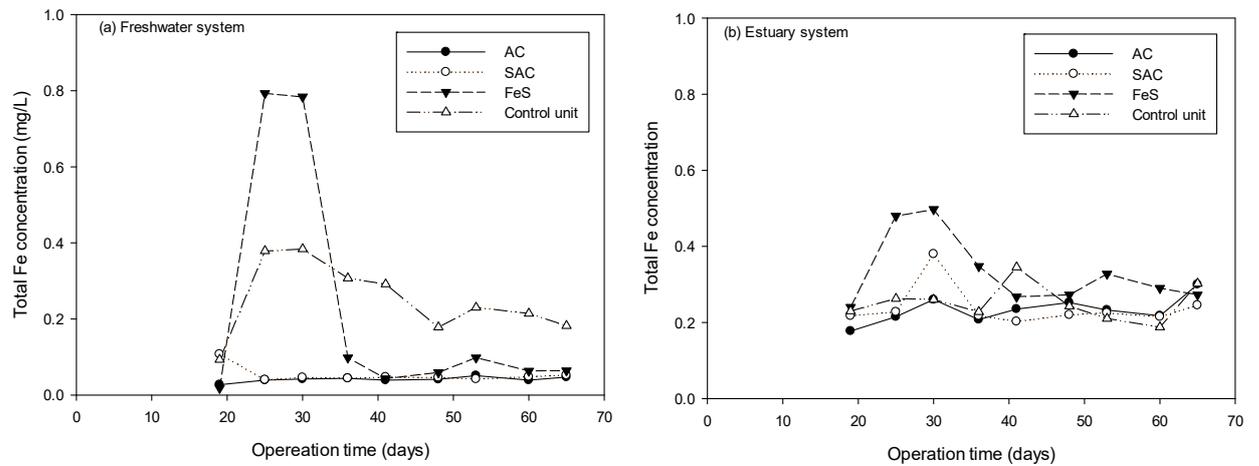


Figure S9. The total Fe variation of microcosms in (a) freshwater system and (b) estuary system