Controlling CH4 Emissions from Integrated Vertical-Flow Constructed Wetlands by Using Potassium Peroxymonosulfate (PMS) as Oxidant

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Controlling CH_4 Emissions from Integrated Vertical-Flow Constructed Wetlands by Using Potassium Peroxymonosulfate (PMS) as Oxidant

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Abstract

It is very important to control methane emissions to reduce global warming. In this study, an attempt was made to adjust the oxidation-reduction potential (Eh) by adding different mass of potassium peroxymonosulfate (PMS) (0 g, 31.25 g, 62.5 g, 125 g, 250 g and 500 g) to reduce methane from integrated vertical-flow constructed wetlands (IVCW). Results show that the reduced CH_4 emission from IVCW was the highest with decreased by 43.5% compared to blank group (PMS=0), when adding 125g PMS. Importantly, the reduced CH_4 from the root-water system of IVCW was higher than that of the stem-leaf system of IVCW, when adding PMS. It's found that Eh not only has a significant correlation with CH_4 flux, but also has a significant relationship between PMS quality, DO, water temperature and sampling time (y_{Eh}= -0.44X_{PMS} + 6.82X_{DO} + 0.38t - 264.1, R^2 = 0.99). It concludes that PMS, as an oxidant, is a very feasible method for controlling methane emissions from IVCW. Further research may combine other

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methods such as microbiology, physical control and hydrology control for mitigating the CH_4 emissions from constructed wetlands.

Keywords: Control of Methane Emissions; Integrated Vertical-flow Constructed Wetland (IVCW); Peroxymonosulfate (PMS); Redox Potential (Eh); *Cyperus alternifolius L.*

1. Introduction

Methane (CH_4) is considered the most important greenhouse gas after CO_2, and constructed wetlands (CWs) are also one of the sources of methane emissions. Annual global emissions of methane from wetlands is about 200 kg CH_4/ha (Kadlec, 2008; Mander et al., 2014; Maucieri, 2017). CH_4 is produced by methanogens under anaerobic conditions and then oxidized and migrated by microorganisms under a series of effects, and the wetland system just provides an anaerobic environment for methanogens (Brinson, 2008). The CH_4 released by CWs is mainly transmitted to the atmosphere through plant aeration tissue and vacuole diffusion. Studies have shown that 70% of the CH_4 produced by CWs is mainly transported by vascular plants, and oxygen will be transported to plant roots under photosynthesis, providing an oxygen environment for root microorganisms and a growth environment for methanotrophic bacteria (Chowdhury and Dick, 2013a). At the same time, CH_4 produced by methanogens in the wetland transmits through the stems and leaves of plants into the atmosphere. Generally, controlling of CH_4 emission from CWs includes three processes of methane production, methane oxidation, and methane release, and ultimately affects the climate change (mainly the greenhouse effect). Therefore, finding feasible ways to control CH_4 emissions during wastewater treatment has received increasing attention (IPCC, 2013).

The control of methane emissions in CWs can generally be divided into macro-control and

50 micro-control. Macroscopically, it includes physical methods (such as aeration, groundwater level
51 control and hydrological changes), chemical methods (such as redox control, iron control, and
52 chemical addition) (Liu et al., 2012; Maltais-Landry and Maranger, 2009). Hydrological methods
53 (Puyuelo et al., 2014)(e.g. groundwater level control and hydrological changes), biological
54 methods (e.g. antibiotic application, vegetation and plant species changes (Cattani and Maccarana,
55 2016)), and environmental controls (e.g. substrate changes, water quality parameters and
56 temperature, or a combination of the above (Molle P, 2008)) have been reported. Microscopically,
57 although the controlling of methane emissions includes molecular methods (Lange and Ahring,
58 2001; Liikanen et al., 2006) and nanostructure control (Hirasawa et al., 2008), it does not apply to
59 CH_4 control in CWs in engineering practice so far.
60 CH_4 emissions are generated by methanogens using organic matter under anaerobic
61 conditions (affected by substrate and hydrological conditions) and partially consumed by
62 methanoxidizing bacteria in the oxidation layer, and finally transmitted from the soil to the
63 atmosphere by means of plant aeration tissue diffusion (Joabsson et al., 1999). Macroscopically,
64 methane emissions from CWs are mainly affected by wetland substrates, wetland vegetation,
65 hydrological conditions, climate, and organic matter content. At present, report not only shows
66 the impact of methane and nitrous oxide emissions in CWs with different texture types of
67 substrates (sand, sandy loam, gravel, clay, peat, etc.)(Sakata et al., 2015; Wu et al., 2015), but
68 also presents that different media affect methane yield. In terms of plants, the selection of plants
69 in CWs usually follows the following principles: suitable species, strong purification ability,
70 developed root system, reasonable mix, high ornamental value and economic value (Xu et al.,
71 2013). The survey illustrates that the vertical-flow constructed wetland system with windmill
72 grass has an increase of 4.9g in the aboveground part of the TP（Total phosphorus）

accumulation for each 1000g increase in biomass (Cui et al., 2011). *Cyperus alternifolius L.* roots are developed, with large biomasses and long growth time, and can grow in winter for a certain period of time (Cui et al., 2011). In the matter of organic matter, when the carbon-to-nitrogen ratio in feed reaches 5: 1, methane emissions are very low (Szafranek-Nakonieczna and Stępniewska, 2015). Artificially added metal elements/cations (such as active Fe (III), solid phase Fe (II)), or non-metal/anions (such as nitrogen load, sulfate (SO_4^{2-}, NO_3^- concentration)), will affect CH_4 emissions (Yan C, 2012). To control methane emissions, it's found that increasing content of iron can promote the oxidation of organic carbon and reduce the amount of methane produced (Beal et al., 2009; Chowdhury and Dick, 2013b; Eric et al., 1996). It's reported that manganese (IV) ions can hinder the oxidation of methane under anaerobic conditions in rice fields, and promote the oxidation of methane under aerobic conditions. Although these chemical control methods are simple and effective, some still bring a certain burden on the environment (Kumaraswamy et al., 2001). From previous research from us in point of hydrological conditions, average methane emission flux from integrated vertical-flow constructed wetland (IVCW) was the smallest when the water depth was 105 cm (Liu et al., 2018). In addition, water temperature can also change the physical and chemical properties of methanogens in the wetland system, thereby affecting the production of methanogens (Inglett et al., 2012a). Water temperature is the most significant of all environmental factors affecting methane emissions ($R^2 = 0.88$) (Johansson et al., 2004). The optimal temperature for methane oxidation is 25°C, but methane can be oxidized at both polar temperatures (-25°C) and high temperatures (30°C), thus it is difficult to control methane emissions by adjusting the temperature (Sitaula et al., 1995). Aeration control could reduce methane emissions from CWs (Maltais-Landry et al., 2009). Aeration control method has a certain effect on CH_4 reduce

without damaging to environment, but the spatial arrangement and usage control of aeration are more complicated. Therefore, it is necessary to find a low-cost and effective method that does not pollute the environment to control methane emissions from CWs. Hydrological control methods have a certain effect on CH_4 emission and have a greater impact on Eh, which the Eh value and wetland methane emissions show a significant correlation (Chowdhury and Dick, 2013a; King, 1990). This shows that as long as Eh is controlled, methane emissions can be controlled to a certain extent. Eh value of -150 mV is the key point of methane production, which the lower of Eh is, the larger methane emissions are. The best Eh range for methane production is -315~-500 mV (Jee and Nishio, 1987; Masscheleyn et al., 1993). Of course, it can adjust the Eh values in CW by adding chemicals such as oxidants. Some scholars have found that after potassium permanganate has been added, the redox potential of groundwater rises immediately, and the higher the amount of potassium permanganate is, the higher the corresponding redox potential is (Copeland and Lytle, 2014; Turan et al., 2018). Additionally, persulfate has a strong oxidizing ability, including of destroying the cell wall of microorganisms, releasing organic matter in microorganisms, and killing microorganisms in the water. None of its oxidized substances produced toxic intermediate substances to the water environment during the reaction when adding persulfate. In summary, adding persulfate to control Eh to control methane emissions will not pollute the environment and is very suitable for use in constructed wetland water treatment systems. In addition to persulfate, many environmental factors also affect the Eh value (for example, water temperature, pH, dissolved oxygen, etc.)

Research has shown that Eh and water temperature and Eh value showed a good linear relationship ($R^2 = 0.99$) (Hou et al., 2014). In addition, dissolved oxygen (DO) also has a positive effect on the Eh value. It's demonstrated that DO is significantly positively related to the Eh

119 value when DO is from 0.1 to 0.5 mg/L, but Eh increases slowly under higher concentrations of
120 DO (Liu et al., 2012). Nevertheless, to date, there is still less control information of methane
121 emissions from CWs by regulating Eh factor.

122 The objectives of this study are: (1) to investigate the Eh variation by adding PMS into
123 IVCW for reducing methane emissions. (2). to monitor the methane emission from IVCW with
124 Potassium peroxymonosulfate (PMS) added. (3) to determine methane control effects on PMS.

125 # 2. Materials and Methods

126 ## 2.1 Integrated vertical-flow constructed wetland and PMS dosing device

127 IVCW (3600mm length×1200mm width×1200mm depth) is composed of an inlet tank and
128 an outlet tank connected with a perforated pipe. The two parts are vertical flow constructed
129 wetlands with opposite water flow directions (as shown in Fig.1), thus forming a "composite
130 "vertical flow constructed wetland, with the same structure and treatment devices, including
131 dimensions, inlet and outlet, substrate (gravel), plant (*Cyperus alternifolius L.*) and methane gas
132 collection system (root water in the inlet tank Subsystem, the root water system in the outlet tank,
133 the stem and leaf system in the inlet tank, and the stem and leaf system in the outlet tank) (see Fig.
134 1 from our previous report (Liu et al., 2018)). In the structure of IVCW, five PMS injection ports
135 are set above five PVC pipes (as shown in Fig.1b). The IVCW 0 is the blank group without
136 potassium peroxymonosulfate (PMS=0 g), and the IVCW 1 and IVCW 2 is used to control methane
137 emission by addding PMS.

138

139 Fig. 1 Schematic diagram of IVCWs. (a) Cross-section of IVCW; (b) Holes distribution of
140 PMS added; (c) Overview of IVCWs.
141

2.2 Experimental design and operation

This field experiment uses artificial sewage to simulate rural non-point source domestic sewage. The components of artificially configured domestic sewage are CH_3COONa, $C_6H_{12}O_6 \cdot H_2O$, NH_4Cl, KH_2PO_4, $MgSO_4$, $CaCl_2$, $(C_6H_{10}O_5)_n$, $(NH_4)_2SO_4$, Na_2CO_3, and Extractum carnis, Protein, the influent sewage concentration is TC (141.04 ± 19.5 mg/L) ,TN (13.22 ± 1.83 mg/L),TP(0.92 ± 0.04 mg/L),TOC(112.85 ± 27.22 mg/L),COD(433.08 ± 32.83 mg/L) (Cui et al., 2007). Sewage was directly conducted to IVCW by inlet, and was discharged by outlet after sewage treating and methane controlling by PMS added.

PMS is used to control methane emissions in this study. PMS has a chemical formula of $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4 \cdot Na_2O$. Main active ingredient is $KHSO_5$. The reaction formulas are as follows:

$$KHSO_5 \rightarrow HSO_5^- + K^+ HSO_4^- + [O] + K^+ \quad (1)$$

$$HSO_4^- \rightarrow gSO_4^- + H^+ \quad (2)$$

$$gSO_4^- + H_2O \rightarrow SO_4^{2-} + gOH + H^+ \quad (3)$$

Hydrolysis of PMS produces [*O*], hydroxyl radical (•*OH*) and sulfate radicals (•SO_4^-) with certain oxidative properties. In the first experiment try, mass of 125g PMS was added to the IVCW for pre-experiment of methane control. It was found that the addition of 125g PMS can maintain the lowest Redox potential (Eh) of IVCW for 7 days, resulting in Eh values ranged from -159 mV to 188 mV. It indicates from pre-treatment experiment that the PMS pose of 125 g can significantly stimulate and improve Eh values in IVCW. Therefore, based on the experimental results of 125g PMS, five PMS mass gradients of 31.25g, 62.5g, 125g, 250g and 500g were set in the form of a geometric sequence and added to the IVCW to monitor the quality

of each layer of the IVCW. Each designed mass of PMS is averagely added to each injected hole of PVC pipes (Fig. 1b).

Based on optimal hydrology parameter of water depth of 105 cm from our previous research results (Liu et al., 2018), the designed experiment time of PMS to control methane in IVCW is July to December, and the monthly PMS addition amount from July to October is 31.25g, 250g, 61.25g, 125g,500g PMS is added from November to December, while the blank experiment is monitored simultaneously from July to December. The experimental operation processes included six steps are the same to our previous report (Liu et al., 2018). The experiment time of each group was carried out by adding PMS to IVCW 2, and the blank (control) experimental system of IVCW 0 without PMS was simultaneously compared. When the Eh value of the third layer of IVCW is lower than -100 mV and no longer increases, the experiment stops.

2.3 Samples, measurement and data analysis

The monitoring of CH_4 samples is same to previous research (Liu et al., 2018), including CH_4 monitoring of root-water subsystem in the influent tank, rootwater subsystem in the effluent tank, stem-leaf subsystem in the influent tank, and stem-leaf subsystem in the effluent tank. Water samples are collected at the sampling spots (see Table 1 of Liu (Liu et al., 2018)), and are simultaneously monitored when sampling and monitoring of the CH_4 samples. Eh, water temperature, conductivity, salinity and DO are immediately measured on-site when sampling water and CH_4. Based on the "Water and Wastewater Monitoring and Analysis Methods"(SEPA, 2002), CH_4 was measured by a portable soil gas flux measurement system (WS-LI820, WEST Systems, Italy)；Eh is measured with a pH meter (PB-10); temperature, conductivity, TDS and salinity are measured with a portable conductivity (DDBJ-350 (06)); DO is measured with a portable instrument (HI98186).

188 The data on methane fluxes are processed by using Flux Revision professional software,
189 which is provided by a portable soil gas flux measurement system (WS-LI820, WEST Systems,
190 Italy). Data statistical analysis and graphing are done by software R (R Foundation for Statistics
191 Computing, version 3.3.1, Copyright (C) 2016) and SPSS (Statistical Product and Service
192 Solutions, version 27.0), The main analysis methods are PCA (Principal Component Analysis),
193 regression analysis and Pearson correlation analysis.

194 # 3. Results

195 ## 3.1 Methane emissions from IVCWs by PMS regulation

196 Variations of methane flux from IVCWs are presented in Fig. 2. The average methane flux
197 of IVCW with PMS added during the entire experimental period was 0.956 mol/m^2/day. Methane
198 emissions from all IVCWs by adding PMS were reduced by an average flux of 0.170 mol/m^2/day,
199 compared without PMS. Methane emissions from the root-water system of IVCW by adding PMS
200 were reduced by an average flux of 0.158 mol/m^2/day, while the methane emissions from the stem-
201 leaf system of IVCW by adding PMS were reduced only by an average flux of 0.012 mol/m^2/day.
202 Fig. 2a shows the relationship between methane fluxes and mass of PMS added. This demonstrates
203 that the addition of PMS has a certain impact on methane emissions. In addition, in the blank group,
204 the methane emission from the stem-leaf system of IVCWs was 0.88 times than that of the root-
205 water system, while the methane emissions from the stem-leaf system of IVCWs was 1.178 times
206 than that of the root-water system by adding PMS. It can be seen that the reduced methane
207 emissions by adding of PMS from root-water system of IVCWs were significantly higher than that
208 of stem-leaf system.

209

210 Fig. 2 Methane variations with time and PMS dosage. (a) Methane flux and PMS dosage; (b)

Methane flux from July to December.

Methane emissions of IVCWs from July to November are shown in Fig. 2b. CH_4 flux in the blank group was 2.28, 0.75, 1.67, 1.59, 1.2625 times than that of the PMS group (31.25 g, 62.5 g, 125 g, 250 g and 500 g), respectively. Obviously, CH_4 flux from IVCWs during the summer (July-August), was at a relatively low level compared with the autumn and winter (September-December). The average methane emissions in autumn and winter were 1.59 times than that in summer.

3.2 Effect of Eh on methane emissions by PMS regulation

The relationship of CH_4 flux from IVCWs among Eh and mass of PMS is illustrated in Fig. 3. Fig. 3a presents the CH_4 flux from IVCWs and Eh values for blank group and PMS groups. It can be seen that the methane emissions from IVCWs had decreased with the increasing values of Eh. CH_4 flux and Eh have following relationships (Equation (4) for in blank group, Equation (5) for in PMS groups, respectively).

$$y=2E^{-06}x^3+0.0002x^2-0.01x+0.17,\ R^2=0.99 \quad (4)$$

$$y=0.69e^{-0.009x},\ R^2=0.88 \quad (5)$$

The relationship of PMS mass and Eh values for blank group and PMS groups from IVCWs is expressed in Fig. 3b. It can be seen that values of Eh in IVCWs was fluctuation with a decreased tendency, with the increase of the amount of PMS. In blank group, Eh in IVCWs was ranged from -150 mV to 65.65 mV, with an average value of -46.52 mV. In PMS group, Eh in IVCWs was ranged from -81.67 mV to 69 mV, with an average value of -24.71 mV. Eh in IVCWs from PMS groups increased by an average value of 14.34 mV than that in blank group.

Fig.3 Relationship of CH_4 flux from IVCWs among Eh and PMS. (a) Variation of methane flux

and Eh values, (b) Variation of Eh values and added mass of PMS.

3.3 Space-time variations of methane emissions from IVCWs

3.3.1 CH_4 flux changes with time when 31.25g PMS is added

CH_4 fluxes from IVCW after adding 31.25g PMS compared with blank group are presented in Fig. 4. It concludes that the methane flux fluctuates greatly with time. In addition, the methane emissions from the influent tank of IVCW with PMS mass of 31.25g added are significantly higher than from effluent tank, indicating that PMS has more effect on CH_4 reduce for effluent tank of IVCW.

Fig. 4 CH_4 emissions from IVCW after adding 31.25g PMS. (a) CH_4 emissions from each subsystem; (b) Total CH_4 emissions.

Figure 4b shows the relationship between the total CH_4 emission of the IVCW stem-leaf system, the total CH_4 emission of the root-water system and the total CH_4 emission flux with time when 31.25g PMS is added. The average CH_4 emission flux of the stem-leaf system is 0.894 mol/m^2/day higher than that of the root-water system. PMS has a significant impact at 18h, 72h and 120h. Under these conditions, methane emissions are reduced by an average of 274%.

3.3.2 CH_4 flux changes with time when 62.5g PMS is added

When adding 62.5g of PMS, methane fluxes of IVCW are shown in Fig. 5. The variations of CH_4 are shown in Table 1. It can be seen that the methane emission flux fluctuates greatly with time. In addition, the methane emissions from the effluent system to which PMS is added are only 0.02 mol/m^2/day different from the inlet system, indicating that the effect is more uniform when 62.5g of PMS is added.

Fig. 5 CH_4 emissions from IVCW after adding 62.5g PMS. (a) CH_4 emissions from each subsystem; (b) Total CH_4 emissions.

Figure 5b shows the relationship between the total CH_4 emissions of the IVCW stem-leaf system, the total CH_4 emissions of the root-water system, and the total CH_4 emissions flux over time when 62.5g PMS is added. The average CH_4 emission flux of the stem-leaf system is 0.127mol/m^2/day smaller than that of the root-water system. Adding 62.5g of PMS had a significant effect at 18h, 40h and 72h, under these conditions, methane emissions were reduced by an average of 60.5%.

3.3.3 CH_4 flux changes with time when 125g PMS is added

It can be seen that the methane emissions from the influent tank of IVCW with PMS are about twice than that of the effluent tank of IVCW, which indicates that PMS has a greater impact on the influent tank of IVCW in Fig. 6a. The variations of CH_4 are shown in Table 1.

Figure 6b shows the relationship between the total CH_4 emission of IVCW, the total CH_4 emission of the root-water system and the total CH_4 emission flux when 125g PMS is added. The average CH_4 emission flux of the stem-leaf system is 0.585mol/m^2/day smaller than that of the root water system. In addition, the result of the blank group is exactly the opposite. Moreover, PMS has significant effects at 48h，60h，72h and 96h. Under these conditions, methane emissions were reduced by an average of 43.5%. The specific changes are shown in Table 1.

Fig. 6 CH_4 emissions from IVCW after adding 125g PMS. (a) CH_4 emissions from each subsystem; (b) Total CH_4 emissions.

3.3.4 CH_4 flux changes with time when 250g PMS is added

It can be seen that the methane emissions from the inlet system with PMS are about 1.27 times that of the effluent tank of IVCW, which indicates that PMS has a greater impact on the

influent tank of IVCW in Fig. 7a. The specific changes are shown in Table 1.

Figure 7b shows the relationship between the total CH_4 emissions of IVCW, the total CH_4 emission of the root-water system and the total CH_4 emission flux when 250 g of PMS is added. The average CH_4 emission flux of the stem-leaf system is 0.198mol/m^2/day higher than the average CH_4 emission flux of the root-water system. The result of the blank group is just the opposite. In addition, PMS has a significant effect at 40h and 48h. Under these conditions, methane emissions are reduced by an average of 131%.

Fig. 7 CH_4 emissions from IVCW after adding 250g PMS. (a) CH_4 emissions from each subsystem; (b) Total CH_4 emissions.

3.3.5 CH_4 flux changes with time when 500g PMS is added

When 500g of PMS was added, the methane emission flux of the stem-leaf system and root-water system, and the stem-leaf system and root-water system of IVCW 2 changed with the sampling time as shown in Fig. 8a. It can be seen that the methane emission flux fluctuates greatly with time. In addition, the methane emissions from the effluent system to which PMS is added are only 0.048 mol/m^2/day different from the inlet system, indicating that the effect is more uniform when 500g of PMS is added.

Figure 8b shows the relationship between the total CH_4 emissions of IVCW, the total CH_4 emission of the root water system and the total CH_4 emission flux when 500g PMS is added. The average CH_4 emission flux of the stem-leaf system is 0.0087mol/m^2/day larger than that of the root water system. The result of the blank group is just the opposite. In addition, PMS has significant effects at 18h and 264h, under these conditions, methane emissions were reduced by an average of 48%.

Fig. 8 CH_4 emissions from IVCW after adding 500g PMS. (a) CH_4 emissions from each subsystem; (b) Total CH_4 emissions.

In summary, the dosages of PMS that have better effects in this experiment are 62.5g, 125g, and 250g, respectively, and the action time is basically within 2 to 4 days. After 62.5g, 125g, and 250g PMS were added in 2-4 days, the methane emission flux was reduced by 42.4%, 49.2%, and 95.1% compared to the blank experiment. After deducting the effect of temperature, the reduction was 23.6%, 29.5%, and 37.3% respectively.

3.3.6 Regression analysis of CH_4 flux and sampling time

Relationships of methane flux (mol/m^2/day) from IVCWs and sampling time (hours) by adding on PMS are presented in Table 1. Through regression analysis, it is found that the regression equations numbered 1, 4, 5, 6, 13, 16, 24, 25, 27, 31, 34, 35 conform to equation (6) (A_1-A_4 are constants). The difference in constants may point to different conditions. The specific formulas are shown in Table 1, and other regression equations that do not meet the formula (6), the main reason will be further discussed in the follow-up experiments of the research group. Also, it can be concluded from Table 1 that the total states of methane emissions from IVCW are as the carbon source in this study.

$$y = 1/(A_1(x+A_2)^2+A_3)+A_4x \quad (6)$$

Table 1. Relationship between methane and sampling time.

3.4 Relationship of methane flux with Eh, temperature and DO

The results of principal component analysis of environmental factors affecting methane emissions are listed in Table 2. The conclusion is that the cumulative contribution rate of the two

principal components is 90.076%, indicating that these factors have a good correlation. PMS, Eh, and Temperature have significant effects on methane emissions. When adding PMS, Eh of IVCW as a function of PMS mass is regressive to equation (7).

$$y_{Eh}=-2E^{-05}x_{PMS}^{3}+0.018x_{PMS}^{2}-3.578x_{PMS}+143.26,\ R^2=0.819 \quad (7)$$

Table 2. Results of principal component analysis

The relationship between Eh and grams of PMS, temperature, DO, and sampling time conforms to equation (8).

$$y_{Eh}=-0.44x_{PMS}+6.82x_{Temp}+16.08x_{DO}+0.38t-264.1,\ R^2=0.99 \quad (8)$$

The relationship between the methane emission flux and the mass of PMS, water temperature and sampling time is following regressive equation (9).

$$y_{CH_4}=0.009x_{PMS}-0.06x_{Temp}-0.008t+2.886,\ R^2=0.869 \quad (9)$$

4. Discussion

4.1 CH_4 emission flux of IVCWS

Average and range of CH_4 fluxes obtained from CWs under the control of PMS in this study are basically lower than that in blank group, but higher than that of other CWs (Table 3). This may be due to different sewage concentrations in the laboratory configuration in each group experiment and various densities of *Cyperus alternifolius L.* In this experiment, the method of adding PMS is susceptible to environmental factors.

Table 3. Typical CH_4 fluxes of CWs in wastewater treatment

From the results of this experiment, there are obvious seasonal changes in methane emissions. Compared with autumn and winter (September to December), the methane flux of

IVCW in summer (July to August) was at a relatively lower level, which is in line with the findings of others (Søvik and Kløve, 2007). However, contrary to the methane emission law of most wetlands, these findings indicate that the methane emission in summer is higher than that in autumn (Chang, 2003; Salimi et al., 2021). The temperature in autumn is usually lower than that in summer (Denning and Kraus, 2011; Duan et al., 2005; Joabsson et al., 1999; Mander, 2003). From the results of correlation analysis in Table 2, temperature is the main controlling factor of CH_4 flux. This is because the PMS added in this experiment is greatly affected by temperature, the higher the temperature, the faster the decomposition, thus suppressing methane emissions. Of course, temperature is an important factor that affects microbial activities, and microbial activities may produce more CH_4 in an anaerobic environment (Keppler et al., 2006). Studies show that the optimal temperature for methanogens is around 35°C (Conrad, 2007; R., 2007; Yao and Conrad, 2000; Zhang et al., 2016), when the atmospheric temperature rises, the amount of methane produced in wetlands also increases (Freeman et al., 2002). The research site of this experiment is at the base on the mountain of Dujiangyan City, Sichuan Province. The average summer temperature during this experiment is only about 32°C, and the water temperature is lower. The activity of methanogens may be limited, which reduces methane emissions. In addition, the status of vegetation in the wetland ecosystem is very important, and the respiration of vegetation is also a key part of the respiration of the wetland ecosystem. The migration of CH_4 from the anaerobic potential in the wetland soil to the troposphere involves many mechanisms, including diffusion, transpiration, and the migration of rooting plants (Søvik and Kløve, 2007).

The results of this experiment show that in the blank group, the methane emissions from the stem-leaf system were 0.88 times than that of the root-water system. This is consistent with the findings of previous investigation from us (Liu, 2019). Because plant root exudates and

abscission (sugars, organic acids, etc.) will become substrates and affect methane emissions (Conlin and Crowder, 1989; Koebsch et al., 2013), and it can be found from Fig. 5 that the methane emissions from the root-water system are significantly higher than those from the stem-leaf system, just when the temperature is high, and the stomata of the stem-leaf may be partially closed at corresponding time. The experimental results show that the methane emission from the stem-leaf system was 1.18 times than that of the root-water system, and there was a positive correlation between salinity and PMS addition (R^2=0.80). This may be due to the increase of salinity can inhibit microbial biomass and activities (Wong et al., 2010), and thus suppress methane emissions. Increased salinity can increase the potential of methane oxidation in the soil, promote the occurrence of methane oxidation, and may eventually reduce methane emissions (Marton et al., 2012).

4.2 Impact of Eh on methane emissions

In the IVCW of this experiment, the Eh of PMS group increased by 14.34 mV on average compared to the blank group. The experimental results show that adding 500gPMS can significantly increase the salinity about 2.75 times that of the blank group, and the Eh value is also significantly reduced, but Eh does not change linearly with the increase of PMS, This may be due to the PMS is a flaky solid, which its decomposition rate was affected by water temperature. This research is a comprehensive field test without any temperature control equipment, and the general laboratory research strictly controls the temperature at about 25°C. In addition, the results show that the average methane flux of the PMS group was 0.171 mol/m^2/day (About 14.5%) lower than that of the blank group, indicating that the addition of PMS had an extent controlling effect on methane emissions.

Results show that methane flux gradually decreased with the increasing of Eh values in this

study. This is consistent with the findings of others (Mishra et al., 1997; Wate., 2007). The change curve of PMS group basically accords with Eq. (5) and the blank group fits the Eq. (4), which have shown that the activity of methanogens in substrates was affected by Eh values, and methane production depends on lower Eh values (Inglett et al., 2012a). It's has been reported for methane production that the optimal range of Eh was -315~-500 mV (Jee and Nishio, 1987). It also has indicated for methane production that the optimal Eh value is -150 mV (Masscheleyn et al., 1993), and the methane production amount is larger when Eh is lower than this value. Relevant research shows that methane is produced only when the soil Eh is -140 mV. When the soil Eh ranged from -200 mV to -300 mV, methane production increases by 10 times and emissions are increased by 17 times (Liu et al., 2014).There are also reports that methane is produced when the soil Eh is below +240 mV, and the critical Eh value of methane production is higher than previously reported (Szafranek-Nakonieczna and Stępniewska, 2015). These studies indicate that the critical condition of Eh produced by methane is not necessarily -150 mV. Therefore, Eh with an average value of -46.52 mV in this study was evidently higher the threshold value of Eh (-150 mV), the methane emission can be efficiently controlled by adding PMS.

4.3 The effects of water temperature and PMS and DO on Eh

The correlation analysis results of the effects of temperature, Eh and DO on methane emissions is presented in Table 4. It can be seen that the correlation between methane and Eh is very significant, indicating that Eh values an important factor affecting methane emissions in IVCW. In addition, the correlation between temperature and Eh is also significant, indicating that temperature is an important factor affecting Eh. These are consistent with the research results of other (Zhang et al., 2016).

Table 4. Correlation analysis between various indicators

Temperature affects methane emissions by affecting Eh. Reports have shown that the rate of methane oxidation and production is greatly impacted by temperature (Liu et al., 2014), while the rate of methane emissions and production in wetland substrate increases with increasing temperature (Bhattacharyya and Neogi, 2013). The principal component analysis results of this experiment show that principal component 1 can explain 65.5% of methane emissions, and the temperature score of principal components 1 reaches 0.82, which plays a certain role in methane emissions, and other studies also found that soil temperature can explain 50.3% to 60.7% of CH_4 emissions from reed wetlands (Kankaala and Ojala, 2004). From the results of the experimental blank group, methane emissions in winter were 0.109 mol/m^2/day lower than in autumn, which can be seen, lower temperatures may cause reduced methane flux. There are possible two main explanations for this phenomenon in current research: (1) Low temperature inhibits the activity of methanogens, resulting in a reduction in methane production. (2) Methane-oxidizing bacteria are less sensitive to temperature than methanogens, and are less affected by low-temperature environments. They are still quite active at 10°C. Therefore, the oxidation of methane oxidizing bacteria, which is still active at low temperatures, exacerbates the decline in methane flux (Hulzen et al., 1999; Jerman et al., 2009; van Hulzen R. Segers P. M. Van Bodegom., 1999). Although the results of this experiment show that methane emissions are related to temperature, the correlation is not significant, which is the same as the result of another (Yuan et al., 2019). This shows that in addition to temperature, there are other environmental factors (such as humidity, DO, etc.) that affect methane emissions.

Results show that DO also affects the Eh value in this study. The relationship between Eh value and PMS grams, temperature, DO and sampling time conforms to Equation (7). Studies have shown that DO does have an effect on Eh (Azizi et al., 2020). In the low DO concentration range of 0.0 to 0.5 mg/L, Eh increases rapidly as DO increases. When the DO is greater than 1.0 mg/L, the Eh value increases (Qiao et al., 2018; Zhai et al., 2012).

5. Conclusions

In order to reduce methane greenhouse gas emissions caused by constructed wetland, PMS was added into the IVCW used for domestic sewage treatment in this study to control the CH_4 emissions. The main conclusions are as follows:

Experimental results prove that adding PMS to control Eh value can achieve the effect of reducing methane emissions from IVCWs. Optimal dose of PMS is 125 g for reducing highest methane emissions. Within 2-4 days after adding PMS dose of 125 g, IVCW methane emissions were reduced by 43.5% compared with blank group. Compared with other reported CWs, the CH_4 emission (0.956 mol/m^2/day) of IVCW in this study is relatively high. In the summer of blank group, the methane emission of the root-water system has reached 63.5%, almost accounting for the main emission. However, the methane emission reduction of the root-water system under the action of PMS is 12.76 times than that of the stem-leaf system, and the reduction of methane emission in summer is higher than that of other seasons. Therefore, the effect of using PMS in summer is mainly to reduce methane emissions in the root-water system. The conclusion of this study is that PMS, as an oxidant, is a very feasible engineering method for mitigating methane emissions from IVCWs.

Author contribution

Hongbing Luo： Research activity planning and execution, Project administration, Funding acquisition, Data curation, Writing- Reviewing and Editing.

Yali Guo：Methodology, Formal analysis, Draw Figures, Writing- Original draft preparation.
Xiaoling Liu：Supervision, Writing- Reviewing and Editing.
Aiping Pu: Research activity planning and execution, Experiment, Data processing.
Ke Zhang: Writing- Reviewing and Editing.
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Data availability The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate Not applicable

Consent for publication Not applicable

Competing interests The authors declare no competing interests.

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728 Table 1. Relationship between methane and sampling time.

IVCW		Number	PMS Mass (g)	CH_4 range (mol/m^2/day)	average CH_4 (mol/m^2/day)	Regressed analysis of CH_4 and sampling time	Result of Carbon Emission
Influent Tank	Stem-Leaf System	1	31.25g	-3.54~8.07	0.494	$y = 1/(-0.14 (x-36.19)^2+2.11)-0.001x, (R^2=0.95)$	Carbon source
		2	62.5g	0~0.332	0.216	$y = 0.30-0.36/(1+(x-20.53)/(-6.46)^2), (R^2=0.86)$	
		3	125g	-0.03~0.532	0.185	$y =-0.338Sin(2\pi x/(-0.55)-2.72), (R^2=0.57)$	
		4	250g	-0.301~1.546	0.282	$y = 1/(0.004(x-180.73)^2+0.21)+0.001x, (R^2=0.60)$	
		5	500g	0~0.815	0.306	$y = 1/(0.0004 (x-122.46)^2+1.53)+0.001x, (R^2=0.32)$	
	Root-Water System	6	31.25g	-4.731~1.851	-0.153	$y = 1/(-0.0002(x+102.13)^2+10.71)+0.001x, (R^2=0.87)$	Carbon Sink
		7	62.5g	0.058~0.694	0.269	$y = (-36.54+x)/(-156.72+4.68x)+ 6E^{-06}x^2, (R^2=0.86)$	Carbon source
		8	125g	0~6.817	0.765	$y = 1/(0.75x-13.29) (R^2=0.97)$	Carbon source
		9	250g	-0.24~0.674	0.179	$y=0.84-0.05x+0.001x^2-4.9E^{-06}x^3+1.34E^{-08}x^4-1.32E^{-11}x^5, (R^2=0.60)$	Carbon source
		10	500g	0~0.889	0.325	$y =0.63(Sin(2\pi x /0.24+0.8))^2, (R^2=0.29)$	Carbon source
Effluent Tank	Stem-Leaf System	11	31.25g	-3.653~4.962	0.124	$y = (-17.07+x)/(-45.04+1.24x)-0.013x (R^2=0.88)$	Carbon source
		12	62.5g	0~0.537	0.215	$y = 0.20Sin(0.43x+0.03)+0.20, (R^2=0.73)$	
		13	125g	-0.048~1.374	0.227	$y = 1/(0.09(x-18.87)^2+0.08)+0.002x, (R^2=0.96)$	
		14	250g	-0.63~1.178	0.229	$y = 1/(-64.95+3.62x+268.09/x)+0.001x, (R^2=0.69)$	
		15	500g	0~0.809	0.305	$y = 1/(-5.13+0.04x+296.28/x)+0.0003x, (R^2=0.30)$	
	Root-Water System	16	31.25g	-2.954~0.970	-0.123	$y = 1/(-0.002(x-58.83)^2+6.7)-0.001x, (R^2=0.77)$	Carbon Sink
		17	62.5g	0~0.615	0.289	$y=0.001x^5-0.02x^4+0.22x^3-1.14x^2+2.53x-1.43, (R^2=0.80)$	Carbon source
		18	125g	0~0.561	0.233	$y = 0.20Sin(0.91x-1.67)+0.21, (R^2=0.62)$	Carbon source

		19	250g	-1.084~1.92	0.133	y =0.45-70.45/x+1683.14/x^2+7539.59/x^3,(R^2=0.69)	Carbon source
		20	500g	0~0.963	0.277	y = -0.007Tan(0.06x-0.02),(R^2=0.29)	Carbon source
Whole IVCW	Stem-Leaf System	21	31.25g	-7.632~4.029	0.618	y = (-28.48+x)/(-4.79+0.003x^2)-3.32,(R^2=0.92)	Carbon source
		22	62.5g	0~0.809	0.431	y = 1/(118.89-4.12x-537.93/x)+0.413ln(x),(R^2=0.54)	
		23	125g	0~1.742	0.413	y = 1/(1727.75(x-60)^2+0.7)+0.32,(R^2=0.73)	
		24	250g	-0.922~1.936	0.511	y = 1/(0.06(x-19.19)^2-2.35)+0.003x,(R^2 = 0.56)	
		25	500g	0~1.623	0.611	y = 1/(0.0002(x-113.13)^2+0.78)+0.001x,(R^2= 0.44)	
	Root-Water System	26	31.25g	-6.173~2.469	-0.276	y = 1/(123.05-7.83$x^{0.58}$),(R^2=0.90)	Carbon Sink
		27	62.5g	0.284~1.059	0.558	y = 1/(-1.78(x-35.78)^2+27.31)+0.53,(R^2=0.63)	Carbon source
		28	125g	0.128~7.14	0.998	y = 1/(0.087x-15.56),(R^2=0.96)	Carbon source
		29	250g	-1.324~2.182	0.312	y=-2E^{-05}x^6+0.001x^5-0.03x^4+0.35x^3-2.02x^2+4.54x-1.64,(R^2=0.69)	Carbon source
		30	500g	0.143~1.852	0.602	y = -0.01Tan(0.26x+0.96)+0.58,(R^2=0.48)	Carbon source
	Totol system	31	31.25g	-13.805~6.479	0.342	y = 1/(0.02(x-42.35)^2-0.07)-0.02x,(R^2=0.60)	Carbon source
		32	62.5g	0.489~1.613	0.989	y = (-28.12+x)/(-24.28+0.03x^2)+0.008x,(R^2=0.56)	
		33	125g	0.237~7.14	1.411	y = 1/(0.35x-6.21),(R^2=0.84)	
		34	250g	-1.394~4.118	0.824	y = 1/(0.06(x-9.59)^2-0.13)+0.004x,(R^2=0.63)	
		35	500g	0.184~2.6	1.214	y = 1/(7.8E^{-05} (x-111.61)^2+0.55)+0.002x,(R^2=0.29)	

Table 2. Results of principal component analysis

Component	Total	Initial Eigenvalue of Variance%	Cumulative %	Component matrix		
				Environmental Factors	Ingredient 1	Ingredient 2
1	3.274	65.487	65.487	PMS	-0.879	0.346
2	1.229	24.589	90.076	Eh	0.912	0.178
3	0.460	9.210	99.286	DO	0.664	0.744
4	0.036	0.714	100.000	Salt	-0.695	0.707
5	$-6.392E^{-17}$	$-1.278E^{-15}$	100.000	Temp	0.820	-0.171

. Extraction method：principal component analysis method.

a. Two ingredients were extracted.

776 Table 3. Typical CH_4 fluxes of CWs in wastewater treatment

Wetland types	Location	Plant cover	Waste-water type	Experimental design		CH_4-flux (mol/m^2/day)	References
Vertical flow constructed wetland	Sichuan	*Cyperus alternifolius L*	Simulated agricultural domestic wastewater	PMS with different grams		0~0.956	This study
Vertical flow constructed wetland	Jiangsu	Calamus	Antibiotic-containing wastewater	Using Microbial fuel cell		0.007~0.009 15% reduction	(XU, 2019)
Vertical flow constructed wetland	Sichuan	*Cyperus alternifolius L*	agricultural domestic wastewater	Using Micro-aeration		0.283~2.012	(Liu et al., 2018)
Horizontal subsurface Constructed wetland	Shanghai	Convolvulus	Natural river water	Compare different flow regimes and substrates	Horizontal push flow (gravel)	$1.5*10^{-5}$ ~$1.365*10^{-3}$	(Yin et al., 2016)
					Horizontal push flow (ceramsite)	$3*10^{-5}$ ~$7.95*10^{-4}$	
					Horizontal baffle (gravel)	$3*10^{-5}$ ~$2.7*10^{-3}$	
					Baffle up and down (gravel)	$1.5*10^{-5}$ ~$1.14*10^{-3}$	
Vertical flow constructed wetland	Chongqing	*Cyperus alternifolius L*	Domestic wastewater	Comparison of manganese ore filler and ordinary gravel filler	manganese ore filler	0~0.0029	(Xu, 2016)
					ordinary gravel filler	0.126~0.159	
A hybrid constructed wetland	Spain	Juncus effusus	The effluent of an up-flow	Compare different wetland types	Free water surface	0.013~0.052	(de la Varga et al., 2015)
					Horizontal subsurface flow	0.021~0.046	
Surface flow wetlands	Canada	*Typha latifolia L*	Mixture of liquid manure and milk-house wash water obtained	Compare different wetland types	surface flow	0.0074	(VanderZaag et al., 2010)
					subsurface flow	0.014	
Three typical constructed wetland	Miho,Ibaraki,Japan	*P. australis*	Domestic wastewater	Compare different wetland types	Free Water Surface	0~0.0549(highest)	(Liu et al., 2009)
					Subsurface Flow	85% reduction (estimated)	
					Vertical Flow	92% reduction (estimated)	
					Combined CW system	70% reduction (estimated)	
Vertical flow constructed wetland	Japan	*P. australis, Z. latifolia, T.latifolia*	Domestic wastewater	Comparison between plants and no plants	Plant	0~1.05	(Wang et al., 2008)
					No-plant	0.01~0.0409	

Horizontal flow constructed wetland	Sweden	*T. latifolia, G. maxima, Spirogyra sp.*	municipal wastewater	Treatment bed containing vegetation zone and non-vegetation zone	0~0.1395	(Picek et al., 2007)
Surface flow constructed wetland	Norway		Domestic wastewater	Unsaturated filters (TF)with light weight aggregates (LWA)	0~0.066	(Søvik and Kløve, 2007)
Coastal Constructed wetland	Shandong	Reed	Paper mill wastewater	Constructed wetland system including pretreatment	0~0.3378	(Li and Tai, 2002)

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792 Table 4. Correlation analysis between various indicators

		CH_4	Temp	Eh	DO	PMS
CH_4	Pearson correlation	1				
	Sig. (2-tailed)					
	N	5				
Temp	Pearson correlation	-0.851	1			
	Sig. (2-tailed)	0.067				
	N	5	5			
Eh	Pearson correlation	-0.897*	0.921*	1		
	Sig. (2-tailed)	0.039	0.026			
	N	5	5	5		
DO	Pearson correlation	-0.623	0.382	0.707	1	
	Sig. (2-tailed)	0.261	0.525	0.182		
	N	5	5	5	5	
PMS	Pearson correlation	0.435	-0.602	-0.572	-0.349	1
	Sig. (2-tailed)	0.464	0.282	0.314	0.565	
	N	5	5	5	5	5

*. Correlation is significant at the 0.05 level (2-tailed)

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Figures

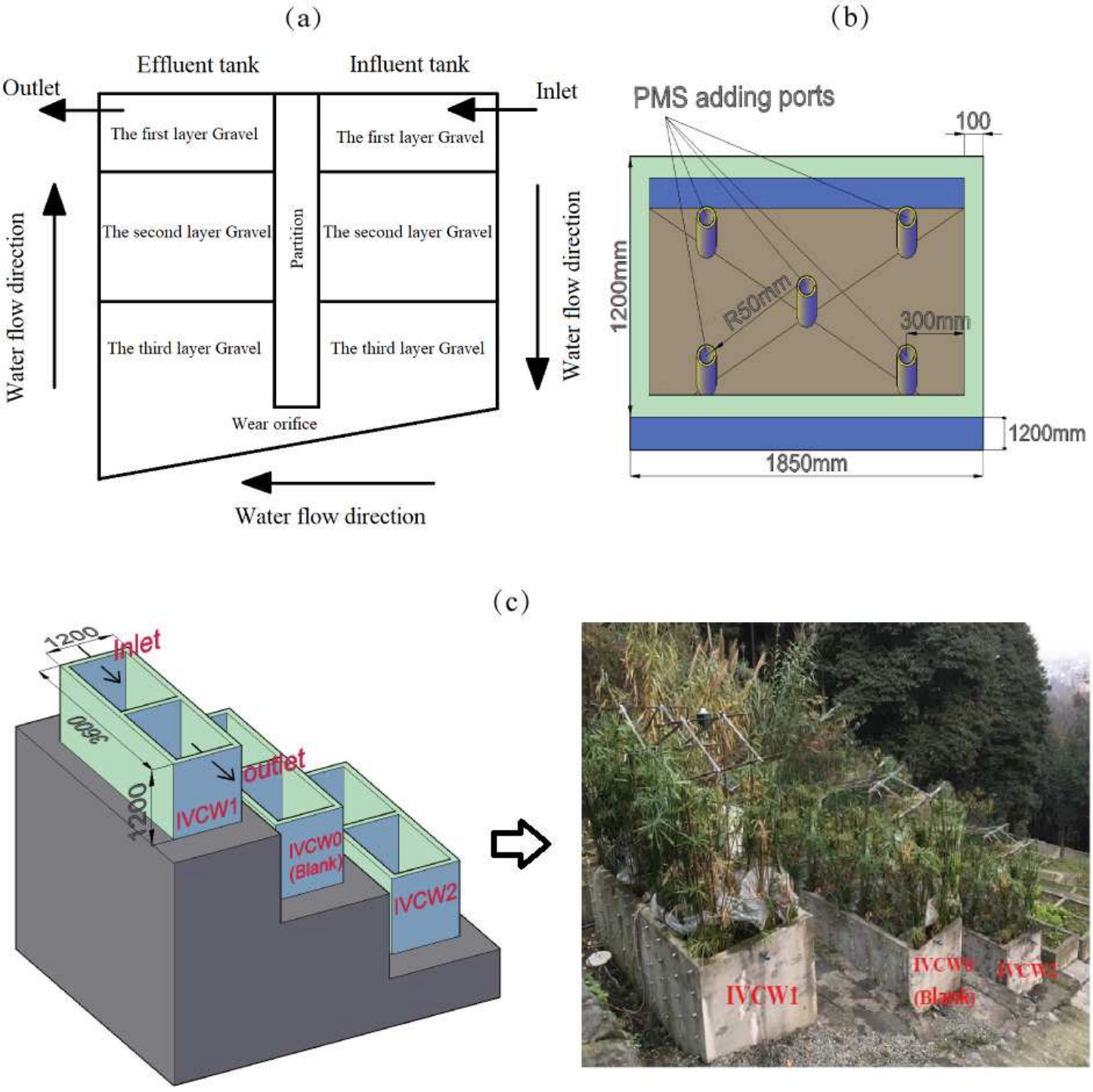

Figure 1

Schematic diagram of IVCWs. (a) Cross-section of IVCW; (b) Holes distribution of PMS added; (c) overview of IVCWs.

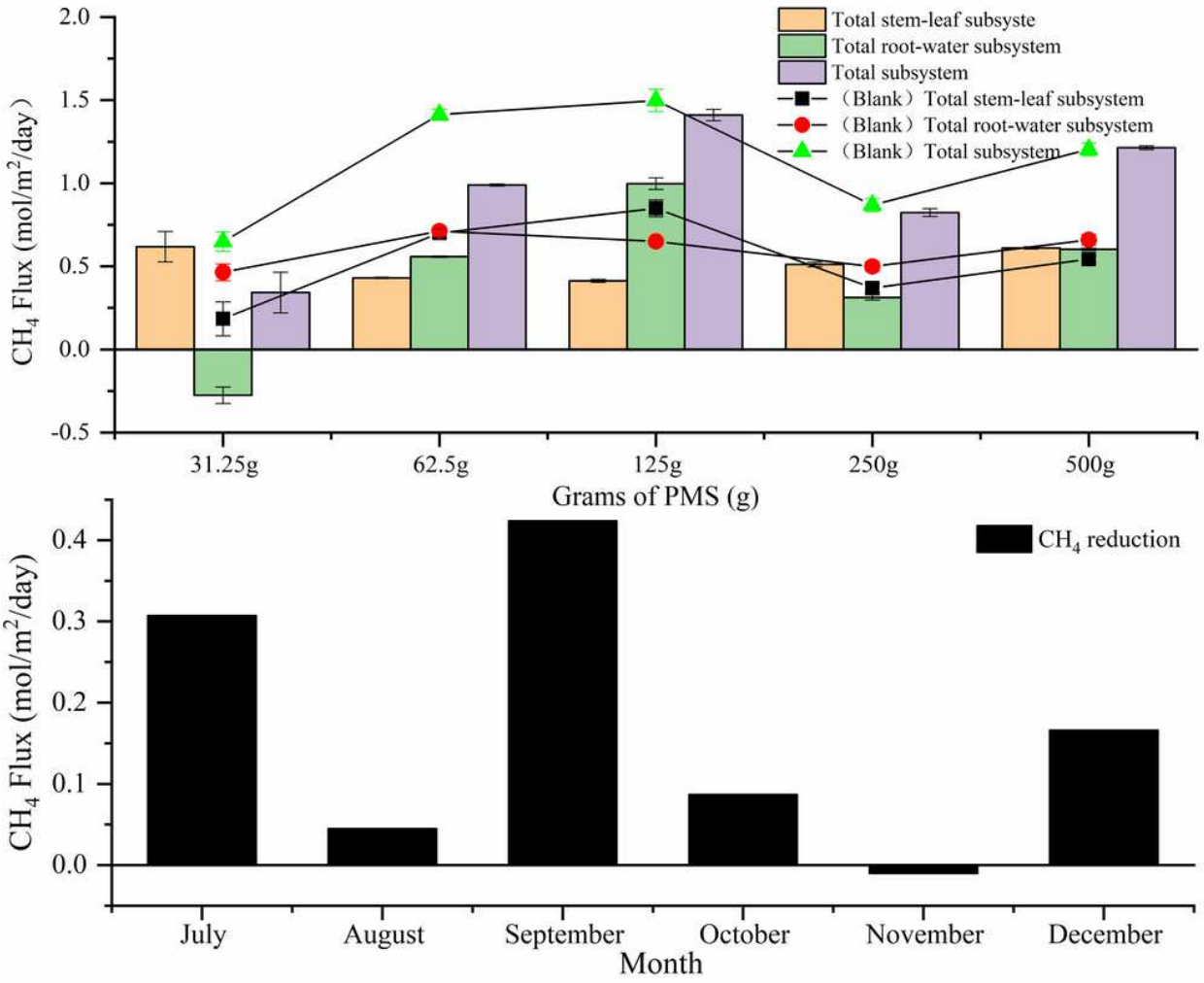

Figure 2

Methane variations with time and PMS dosage. (a) Methane flux and PMS dosage; (b) Methane flux from July to December.

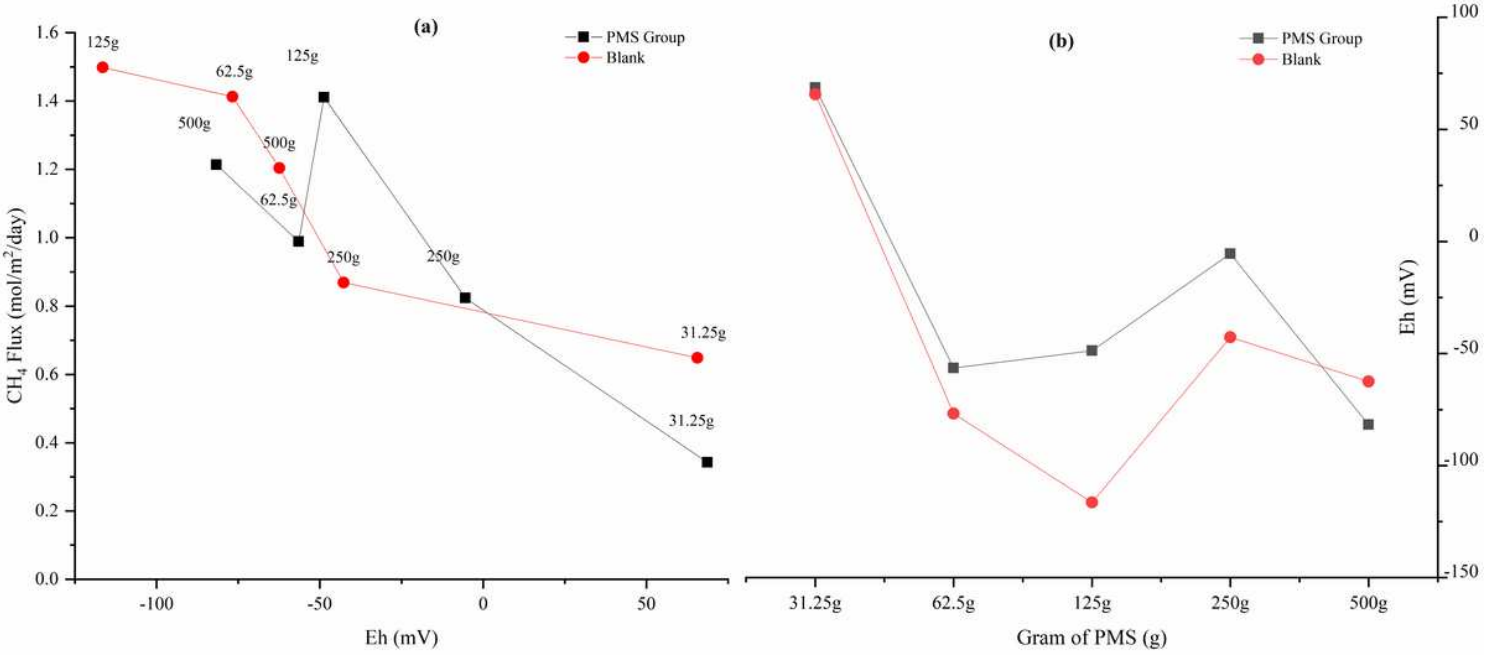

Figure 3

Relationship of CH4 flux from IVCWs among Eh and PMS. (a) Variation of methane flux and Eh values, (b) Variation of Eh values and added mass of PMS.

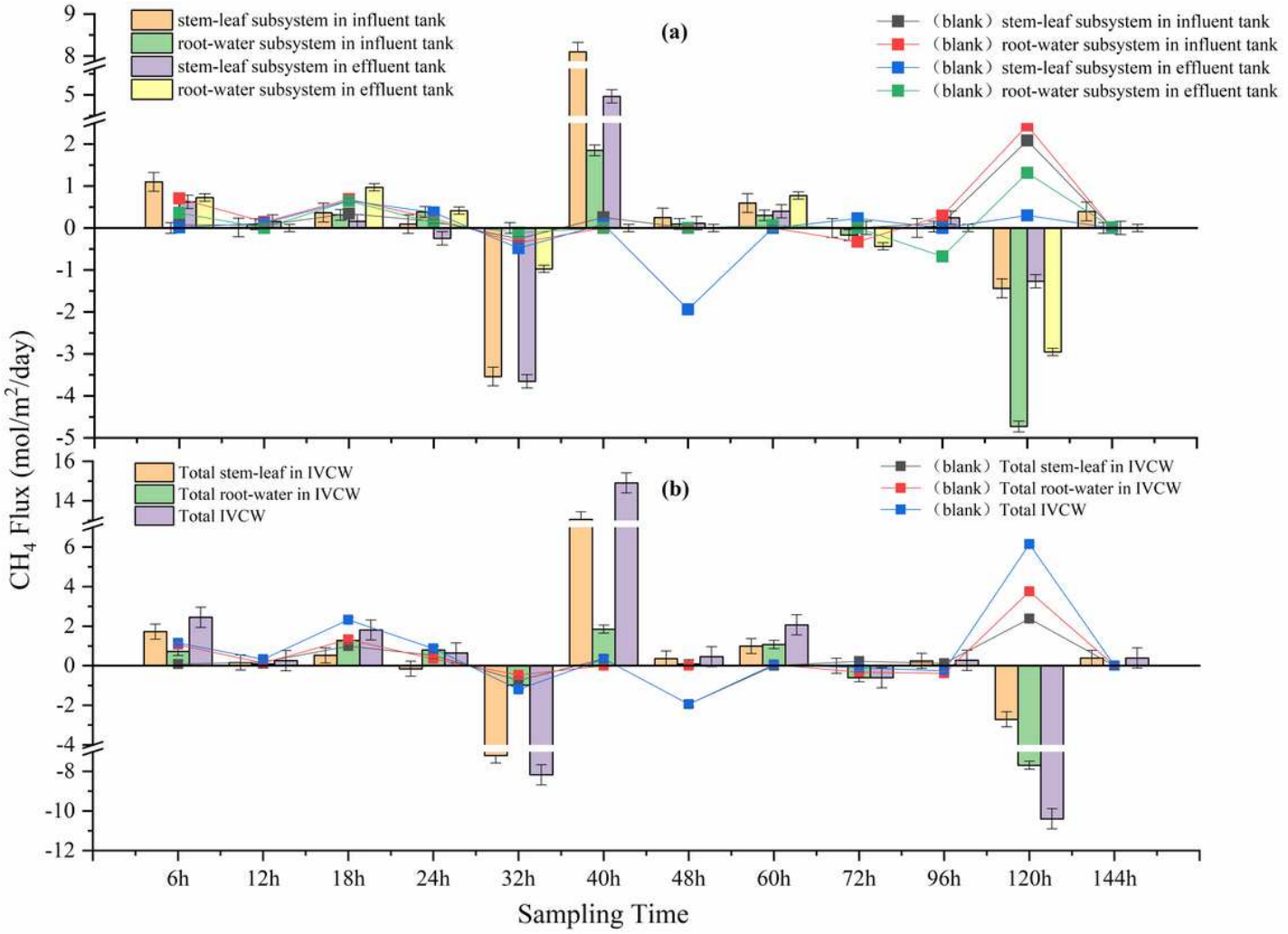

Figure 4

CH4 fluxes from IVCW after adding 31.25g PMS. (a) CH4 emissions from each subsystem; (b) Total CH4 emissions.

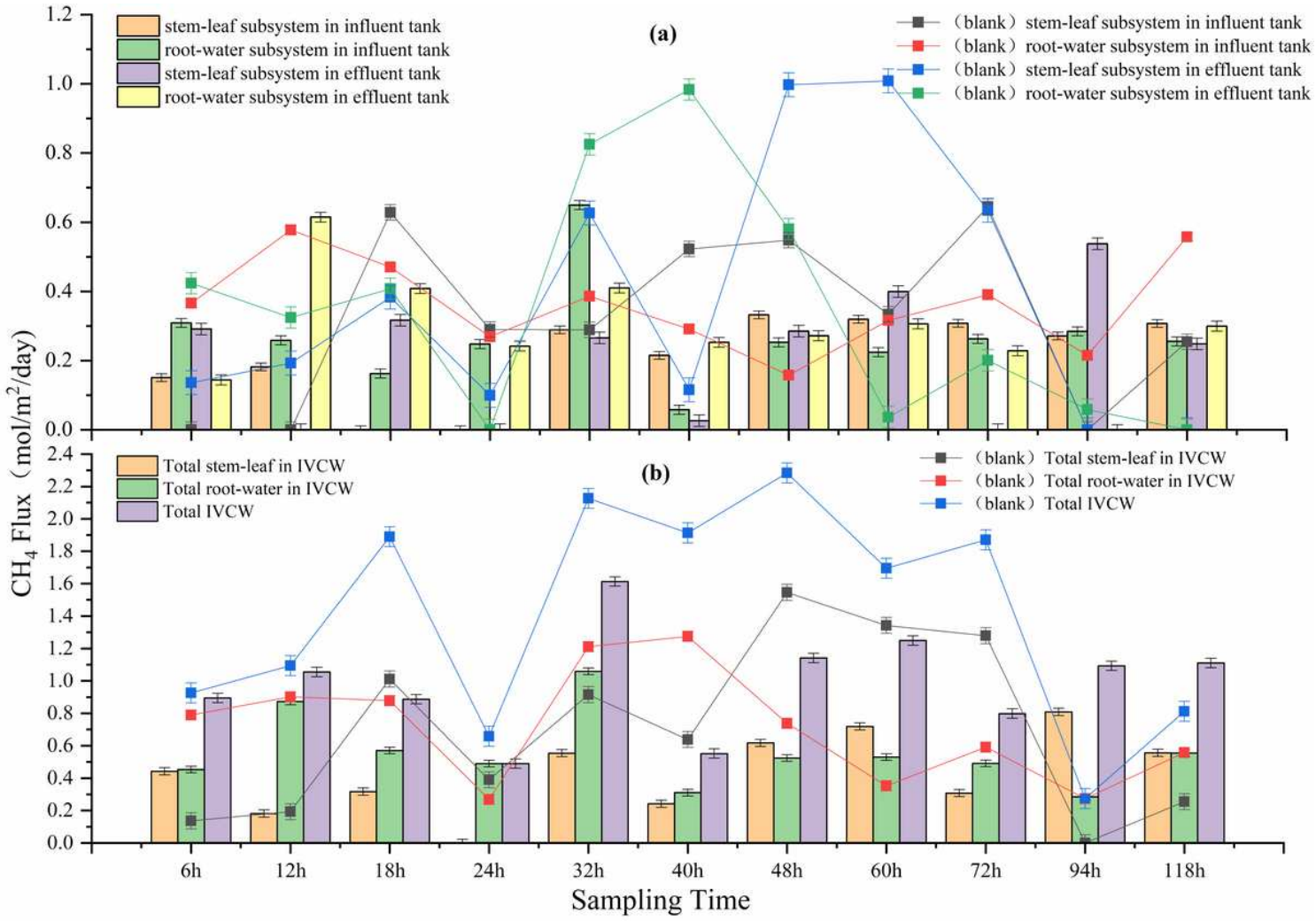

Figure 5

CH4 emissions from IVCW after adding 62.5g PMS. (a) CH4 emissions from each subsystem; (b) Total CH4 emissions.

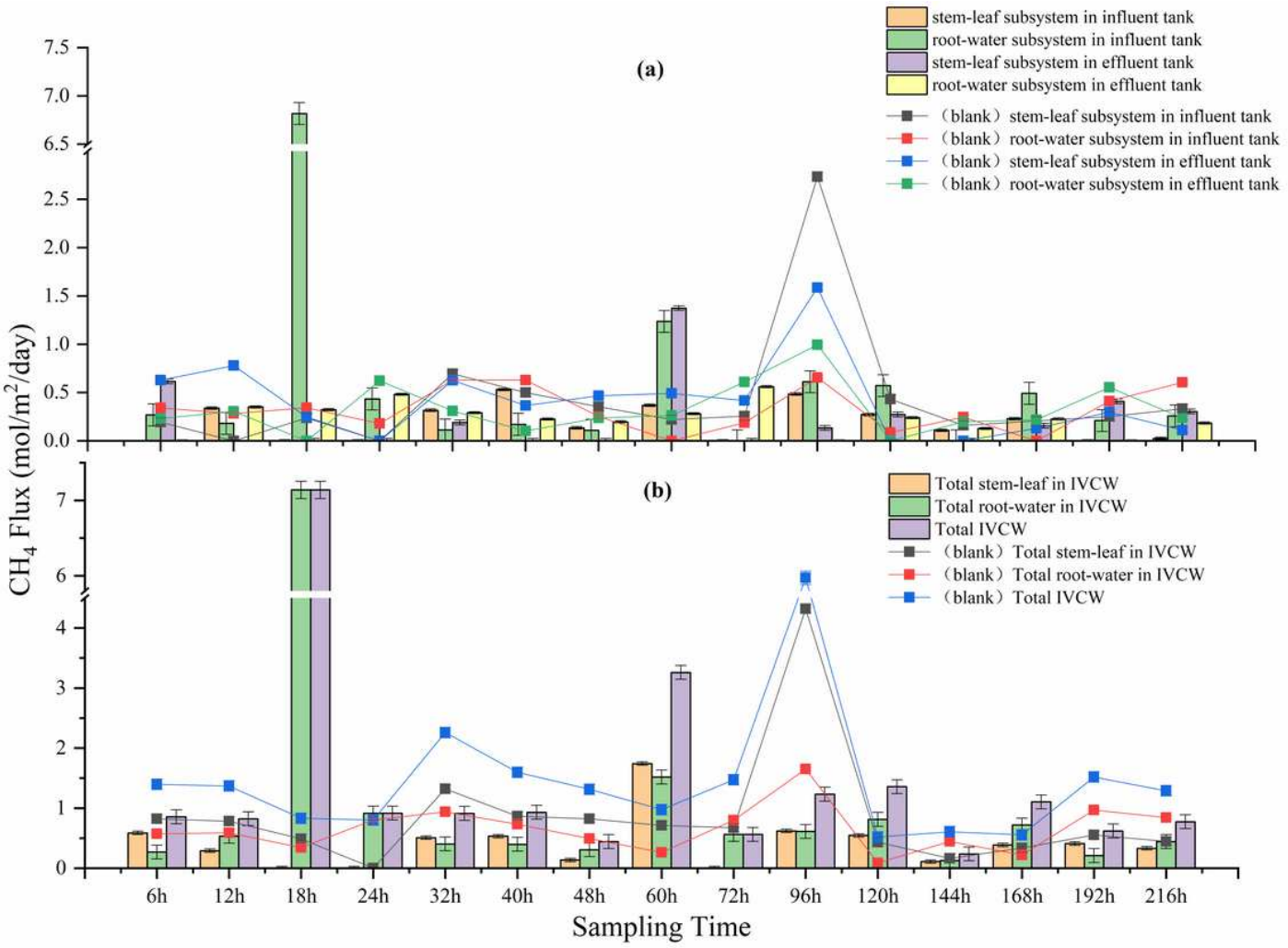

Figure 6

CH4 emissions from IVCW after adding 125g PMS. (a) CH4 emissions from each subsystem; (b) Total CH4 emissions.

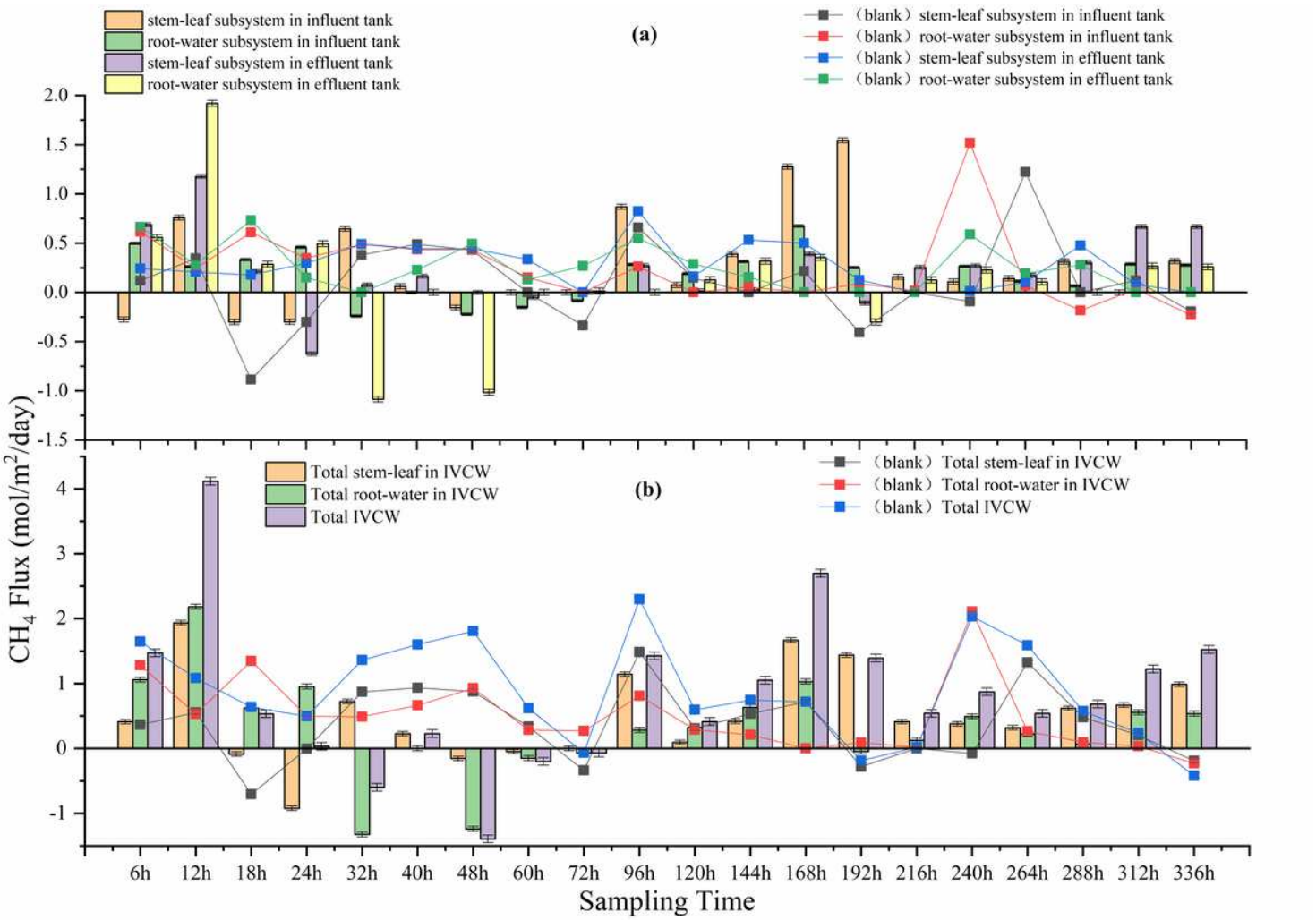

Figure 7

CH4 emissions from IVCW after adding 250g PMS. (a) CH4 emissions from each subsystem; (b) Total CH4 emissions.

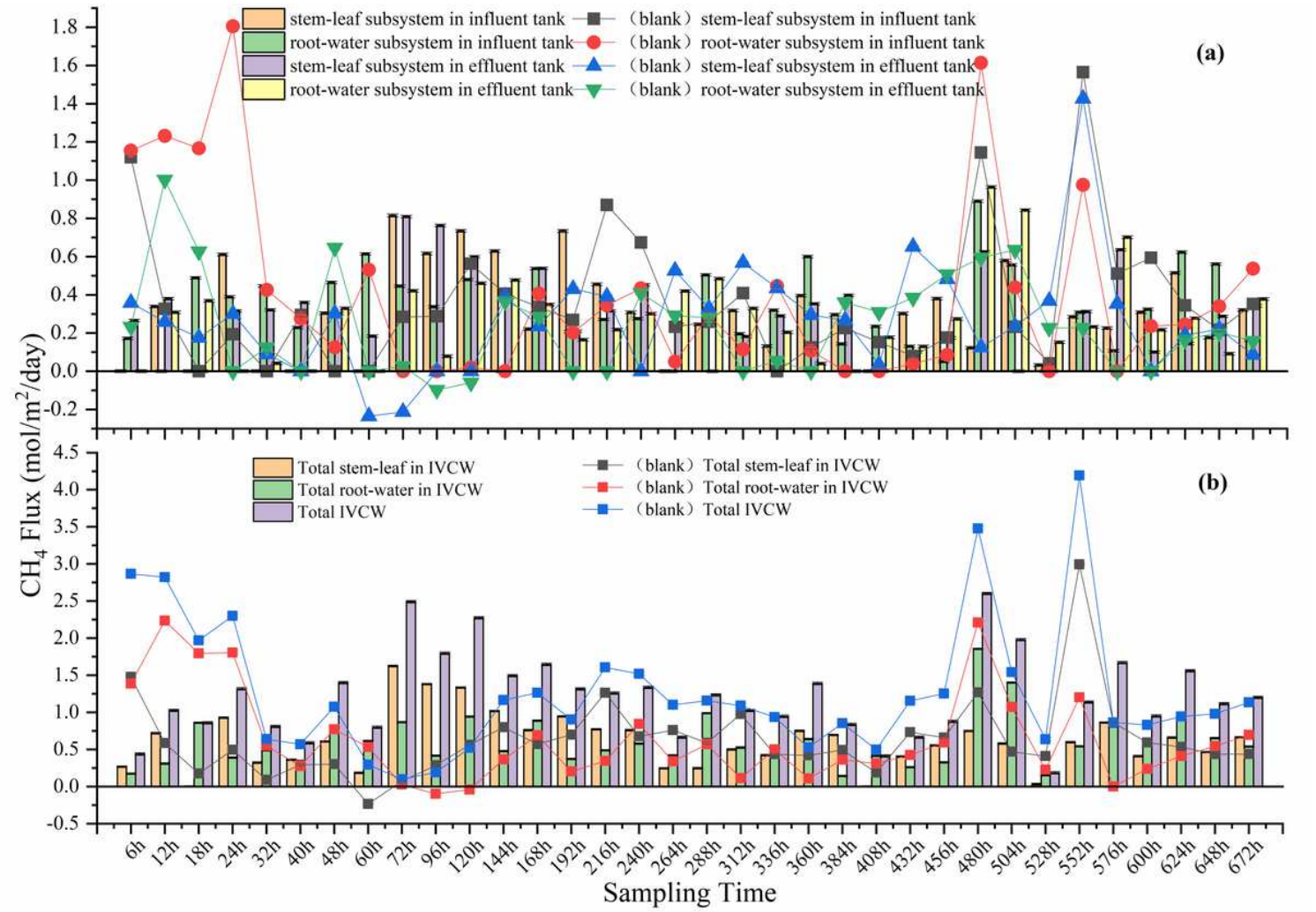

Figure 8

CH4 emissions from IVCW after adding 500g PMS. (a) CH4 emissions from each subsystem; (b) Total CH4 emissions.