Large-scale multi-stage constructed wetlands for secondary effluents treatment in northern China: Carbon dynamics

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Abstract

Multi-stage constructed wetlands (CWs) have been proved to be a cost-effective alternative in the treatment of various wastewaters for improving the treatment performance as compared with the conventional single-stage CWs. However, few long-term full-scale multi-stage CWs have been performed and evaluated for polishing effluents from domestic wastewater treatment plants (WWTP). This study investigated the seasonal and spatial dynamics of carbon and the effects of the key factors (input loading and temperature) in the large-scale seven-stage Wu River CW polishing domestic WWTP effluents in northern China. The results indicated a significant improvement in water quality. Significant seasonal and spatial variations of organics removal were observed in the Wu River CW with a higher COD removal efficiency of 64–66% in summer and fall. Obvious seasonal and spatial variations of CH_4 and CO_2 emissions were also found with the average CH_4 and CO_2 emission rates of 3.78–35.54 mg m^{-2} d^{-1} and 610.78–8992.71 mg m^{-2} d^{-1}, respectively, while the higher CH_4 and CO_2 emission flux was obtained in spring and summer. Seasonal air temperatures and inflow COD loading rates significantly affected organics removal and CH_4 emission, but they appeared to have a weak influence on CO_2 emission. Overall, this study suggested that large-scale Wu River CW might be a potential source of GHG, but considering the sustainability of the multi-stage CW, the inflow COD loading rate of 1.8–2.0 g m^{-2} d^{-1} and temperature of 15–20 °C may be the suitable condition for achieving the higher organics removal efficiency and lower greenhouse gases (GHG) emission in polishing the domestic WWTP effluent. The obtained knowledge of the carbon dynamics in large-scale Wu River CW will be helpful for understanding the carbon cycles, but also can provide useful field experience for the design, operation and management of multi-stage CW treatments.

Keywords: Constructed wetlands; Secondary effluents; Organics removal; Methane; Carbon dioxide

1. Introduction

The issue of water scarcity and deterioration has become a serious concern in the world, and this situation is becoming worse with the rapid urbanization, inadequate water/wastewater purification and management especially in developing countries in past decades (Greenway, 2005). Due to lack of convenient and effective wastewater treatments with lower cost (such as construction investment, operation costs and energy consumption), discharging the majority of untreated wastewater directly into urban rivers is a common practice in many cities and small towns, which leads to the serious pollution of the river basins (Wu et al., 2015a). In addition, in recent years great concern has been growing regarding to the treated effluents, typically effluents from wastewater treatment plants (WWTP) (Vivant et al., 2016; Wu et al., 2017). Such wastewaters contain excessive organic pollutants and nutrients, which are not properly/partially treated, are simply discharged into rivers and estuaries, which may impact aquatic ecosystem health and then pose potential risks to human health (Matamoros et al., 2008; Wu et al., 2016a,b). In order to tackle this environmental concern, additional effective treatments could be employed to purify WWTP effluents and improve the urban river water quality.

In fact, constructed wetlands (CWs), as an efficient and sustainable ecological treatment technology, have been proven to be an effective alternative to traditional wastewater treatment systems. The typical CW is generally comprised of vegetation, substrates, soils, microorganisms and water, and it can remove various pollutants (such as organics and nutrients) from wastewater by means of physical, chemical, and biological mechanisms (microbial degradation, plant uptake, sorption, sedimentation, filtration, precipitation and volatilization etc.) (Saeed and Sun, 2012; Wu et al., 2015a). Particularly, microbial removal mechanism plays a key role in the removal of pollutant in CWs (Mitsch et al., 2013; Meng et al., 2014). Those processes can be influenced by various environmental conditions and operating parameters such as dissolved oxygen (DO), hydraulic retention time (HRT), water depth, inflow loading, water temperature, season and vegetation (Saeed and Sun, 2012). According to the hydrological condition, CWs can typically be divided into free water surface (FWS) and subsurface flow (SSF) wetlands with different technical characteristics. SSF CWs can be further classified into vertical flow (VF) and horizontal flow (HF) CWs. There is another classification for CWs based on the type of wetland plants used. In the past several years, CWs have been widely applied for removing various pollutants in domestic sewage, agricultural wastewater, industrial effluent, mine drainage, landfill leachate, urban runoff, and polluted river water (Wu et al., 2014). In addition, given their low cost and ease operation, CWs have been shown to be able to efficiently remove organic pollutants, nutrients and harmful bacteria from WWTP effluents with aim to improve the water quality and conserve ecological environment of the urban river (Chen et al., 2014; Morvannou et al., 2015). But most of the previous studies were performed in microcosm-scale or pilot-scale CW systems with a small surface area (Vivant et al., 2016; Wu et al., 2015b). Matamoros et al. (2008) investigated the removal of a variety of organic pollutants in a full-scale surface flow CW fed with secondary effluent from a conventional WWTP, and reported that CW was efficient for removing 12 organic micropollutants from WWTP effluent discharged into the River Besos of northeastern Spain. Chen et al. (2014) studied the removal efficiencies and the kinetics of disinfection byproducts in SSF CWs treating secondary effluent, and a high removal efficiently removed of >90% was achieved in laboratory-scale SSF CWs. In a recent study using FWS CWs receiving secondary effluent from a France WWTP, Vivant et al. (2016) found that FWS CWs could be an efficient treatment for extended-spectrum beta-lactamase-producing *E. coli* disinfection of wastewater. However, it should be indicated that the treatment capacity of a single basic CW was still limited for polishing urban rivers receiving large inputs of WWTP effluent. Concurrently, the more application of multi-stage CWs by combining different types of CWs has increased particularly for achieving the greatest potential for wastewater polishing and more stable pollutant removal (Wu et al., 2015b; Kato et al., 2013). This type multi-stage CW has been proved to substantially improve the treatment performance as compared with the conventional single-stage CWs (Vymazal, 2013a). Kato et al. (2013) designed the six multi-stage CWs for treating high-content wastewater in cold climates of northern Japan, and the satisfactory purification was obtained for organics, nitrogen and phosphorus. Jia et al. (2014) constructed a four-stage wetland system for treating a heavily polluted river, and significant improvement in the water quality was observed. Moreover, several important studies on multi-stage CWs have been conducted to treat emerging organic contaminants (such as personal care products and pharmaceuticals), and demonstrated the great capacity of a multi-stage wetland system as a cost-effective alternative or supplementary to conventional WWTP (Avila et al., 2014a, 2014b). Above previous studies have convincingly proved the benefits of multi-stage CWs in the treatment of various types of wastewater, such as dairy, tannery or domestic wastewater, however, further studies reporting their treatment performance on the treatment of effluent from WWTPs are still lacking. Additionally, few long-term full-scale multi-stage CW systems have been constructed and evaluated for organic pollutant purification and processes of WWTP effluents. What is more, considering the sustainability and the potential of greenhouse gases (GHG) mitigation, not enough data are currently available on the dynamics and influencing factors of GHG emissions in the large-scale multi-stage CWs for polishing WWTPs effluent.

Therefore, the aim of this study was to evaluate the carbon dynamics of a large-scale seven-stage FWS CW polishing secondary effluents from a conventional domestic WWTP in northern China. Specific objectives of this study are: (i) to assess the removal performance and variability of organics in the seven-stage FWS CW for polishing WWTPs effluent; (ii) to evaluate spatial and seasonal variation of methane (CH_4) and carbon dioxide (CO_2) emission in this multi-stage CW system; and (iii) to investigate the influence of the key factors (input loading and temperature) on organics removal and CH_4 and CO_2 emission. The results from this study would be helpful in designing multi-stage CW systems in polishing WWTP effluent for urban river water quality improvement as a sustainable wastewater treatment technology.

2. Materials and methods

2.1. Study site description

Fig. S1 presents the site map of the studied CW (the Wu River large-scale CW), which located on the west side of the Yi River in Linyi, Shandong province, northern China at a latitude of 34°51′-35°06 N and a longitude of 118°06′-118°28′E. Wu River large-scale CW as a treatment system for improving river water quality was directly constructed along the riverbed of the Wu River, and Wu River as the downstream of Yi River and Xianni River is currently the main urban drainage channel to receive the treated effluents from a municipal WWTP in Linyi. The climate condition of the study site is warm temperate continental monsoon climate with a mean annual temperature 14.1 °C and an average precipitation of 818.8 mm, respectively

2.2. Large-scale system design and operation

The Wu River large-scale CW is designed as a multi-stage CW and comprises a rubber dam, a distribution ditch, a sequence of seven stages of FWS CWs which are interconnected by using 500-mm concrete pipes and an outlet (Fig. 1). In order to enhancing reoxygenation or reaeration in CW system, several concrete overflow weirs were designed between the fourth wetland unit and the fifth wetland unit of the CW system. The secondary effluent from the municipal WWTP as the influent was directly held by the rubber dam, and flowed into the following FWS CW systems through the distribution ditch. Finally, the effluent from the CW system flowed into the Yi River through the outlet. The total land area of the system was about 8660000 m^2 (over 15000 m long and 120–320 m wide) with the treatment capability of 380000 $m^3\ d^{-1}$. A natural soil layer of the Wu River was used as substrates for the CW system, and the CW system had a 30–50 cm depth of water above the substrate. The theoretical hydraulic retention time (HRT) was around 7 d, and average hydraulic load was 3.5 cm d^{-1}. The CW system was planted with a diversity of macrophyte types which was mainly the dominant native wetland plants included *Phragmites australis (P. australis), Typha orientalis (T. orientalis), Zizania latifolia (Z. latifolia), Nelumbo nucifera (N. nucifera), Nymphaea tetragona (N. tetragona), Potamogeton crispus (P. crispus), Lemna minor (L. minor) and* water hyacinth. The Wu River CW was constructed completely in February 2010 and then operated from May 2010 after a commissioning period (about three months). During the 6-year operation, in order to realize the optimal treatment capabilities of the CW system, a manual harvesting was performed annually in the Wu River large-scale CW in this study, but there was no mechanized harvesting. During the cold period (from November to December) of every year, when the plants (mainly the emergent aquatic plants such as *P. australis* and *T. orientalis*) in the CW become yellow and ripe in late autumn, they were ready for harvest. Specially, the aboveground parts of plants were harvested manually by cutting their upper parts at about 20 cm above the water level. The harvested biomass from the CW was used as a raw material for paper production in the local paper industry. According to the long-term monitor from November 2010 to November 2014 on the quality of the influent of the Wu River CWs, the characteristics of the influent during the operational period is showed in Table 1. The average influent concentrations of COD, NH_4^+-N, NO_3^--N, NO_2^--N, TN and TP were 41.94 mg L^{-1}, 4.61 mg L^{-1}, 5.72 mg L^{-1}, 0.36 mg L^{-1}, 10.69 mg L^{-1} and 0.51 mg L^{-1}, respectively.

2.3. Field sampling and laboratory analysis

Water samples were collected and analyzed weekly from January 2014 to December 2014 to evaluate the efficiency and variability of the Wu River large-scale CW on organics removal. In this study, water samples were collected from nine sampling sites of the CW including $1^{\#}$ (Inflow), $2^{\#}$, $3^{\#}$, $4^{\#}$, $5^{\#}$, $6^{\#}$, $7^{\#}$, $8^{\#}$ and $9^{\#}$ (Outflow) at a depth of 0.2 m using a sampling bottle (Fig. 1), and the detailed coordinates and description of each sampling site of the CW were described in Table 2. All water samples were transferred immediately to the lab and stored at 4 °C before analysis.

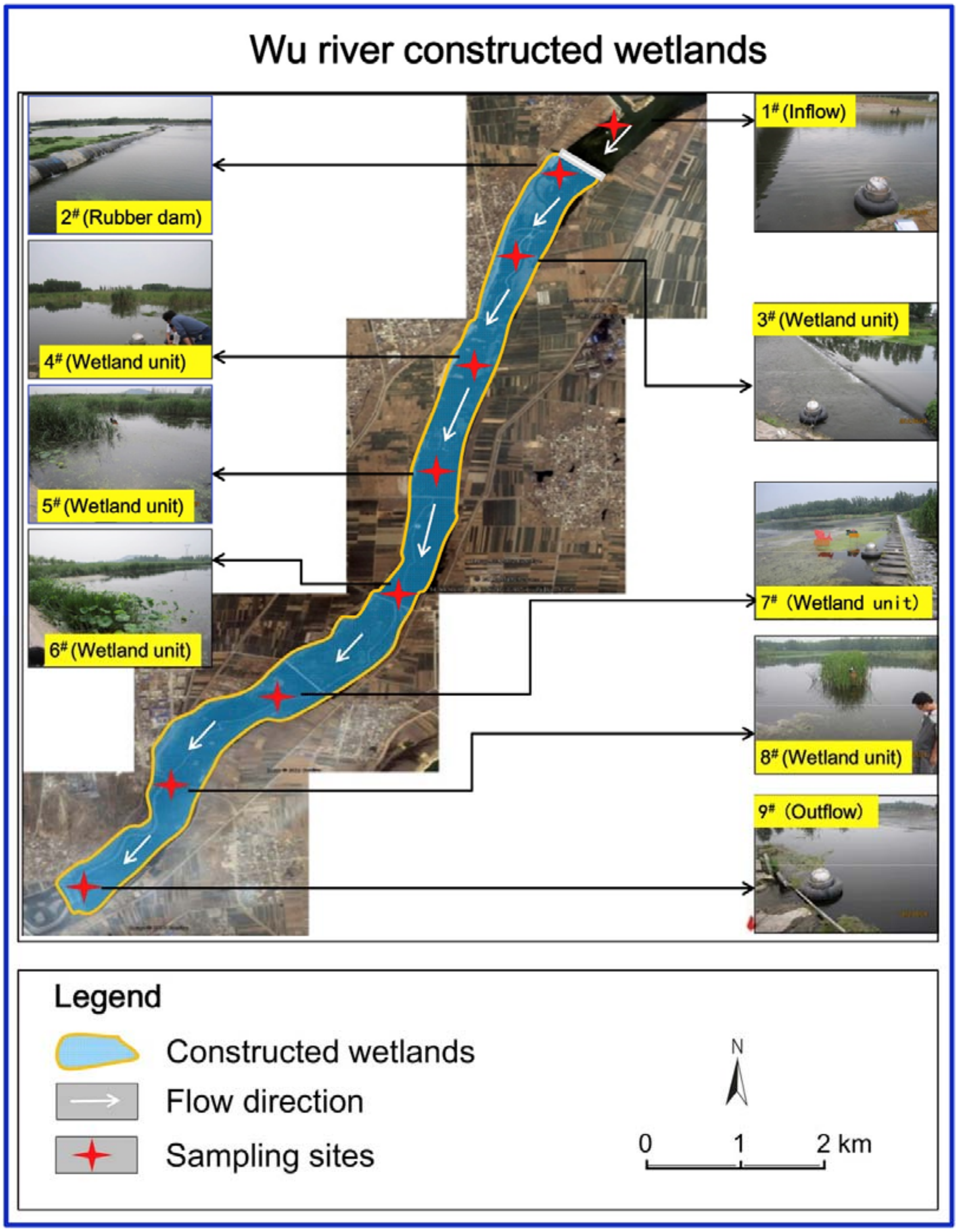


Fig. 1. Schematic diagram of the Wu River multi-stage constructed wetland.

Collected water samples were analyzed for chemical oxygen demand (COD), ammonium (NH_4^+-N), total nitrogen (TN), nitrate (NO_3^--N) and nitrite (NO_2^--N) and total phosphorus (TP). Temperature, pH and dissolved oxygen (DO) were measured in situ by a DO meter (HQ 30d 53LED™ HACH USA) and a glass pH meter (SG2-T SevenGo pro™ MTD, Switzerland). All of the above analyses were performed according to standard methods (APHA, 2005).

Table 1. Characteristics of influent and effluent of the Wu River constructed wetland and design criteria for water quality.

Water quality parameters	**Influent**	**Effluent** [a]	**Effluent requirement (Grade III)** [b]
COD (mg L^{-1})	41.94 ± 8.17	18.44 ± 2.41	≤20
NH_4^+-N (mg L^{-1})	4.61 ± 1.15	1.06 ± 0.92	≤1.0
NO_3^--N (mg L^{-1})	5.72 ± 1.01	4.01 ± 2.15	–
NO_2^--N (mg L^{-1})	0.36 ± 0.19	0.13 ± 0.08	–
TN (mg L^{-1})	10.69 ± 1.06	5.19 ± 2.18	≤1.0
TP (mg L^{-1})	0.51 ± 0.11	0.01 ± 0.01	≤0.2
pH	7.63 ± 0.11	8.71 ± 0.12	6–9
DO (mg L^{-1})	7.13 ± 2.17	19.41 ± 2.72	≥5.0
Water temperature (°C)	18.63 ± 9.51	19.05 ± 11.74	–

[a] The final effluent after the 7 FWS CW treatments.
[b] According to the environmental functions and protective objectives of surface waters, all surface water in Mainland China are divided into five grades, and Grade III means the surface water for drinking purpose, water for aquaculture (common species).

Table 2. The coordinates and description of sampling sites of the Wu River constructed wetland in the present study.

Sampling sites	**Coordinates**		**Environmental conditions**
	Latitude	**Longitude**	
1#	34°52′12.29″N	118°21′01.23″E	With a maximum depth of 0.5 m, and covered with sparse *L. minor* in spring and summer, but with no vegetation cover in autumn and winter.
2#	34°52′01.43″N	118°20′44.01″E	With a depth of 0.3–0.5 m, and covered with dense *L. minor* in spring and summer, but with no vegetation cover in autumn and winter.
3#	34°51′45.16″N	118°20′32.24″E	Open water with a fast water flow rate; Covered with water hyacinth in summer, and withering and dying off in autumn and winter.
4#	34°51′11.94″N	118°20′12.78″E	Covered with *P. australis* (2–3 m in height) during the growing season, but decaying and dying off in winter.
5#	34°50′40.92″N	118°19′59.84″E	Covered with dense *T. orientalis* (about 2 m in height) during the growing season and with a slow water flow rate.
6#	34°50′16.30″N	18°19′46.79″E	The mixed area of *N. nucifera, N. tetragona and P. crispus, and*, but decaying and dying off in winter.
7#	34°49′50.97″N	118°19′14.34″E	Open water with the vegetation of submerged macrophytes, and *N. tetragona* were found in a small area.
8#	34°49′28.02″N	118°18′34.56″E	Covered with *P. australis* and *T. orientalis* with the vegetation height 2–3 m during the growing season, but almost decaying and dying off in winter.
9#	34°48′56.23″N	118°18′04.53″E	Open water with a slow water flow rate and low water depth, but submerged macrophytes were found in some area.

Gas samples were collected from above nine sampling sites of the CW weekly from January 2014 to December 2014, and were analyzed to evaluate the variation of CH_4 and CO_2 emission from the CW. Gas sampling in this study was done using a commercially-available surface emission isolation flux chamber during the experimental period. The surface emission isolation flux chamber was made of a cylindrical stainless steel flux hood with the diameter, volume and sampling area of 0.41 m, 30 L and 0.13 m^2, respectively. Gas samples were collected in 100 ml polypropylene syringes at 10 min intervals for 30 min, and the details of collecting steps of gas samples can be found in the previous studies (Ren et al., 2013). The concentrations of CH_4 and CO_2 were determined using the gas chromatography (SP-6890, China) equipped with a flame ionization detector (GC-FID) and stainless steel packed columns (GDX502). The operating conditions for the GC were: 375 °C reformer temperature, 40 °C oven temperature and 200 °C detector temperature. The carrier gas was ultra-high purity N_2 (30 mL min^{-1}). CH_4 and CO_2 fluxes (mg m^{-2} d^{-1}) were determined from the increase in concentration in the chambers over time with linear regression analysis according to the described method in the previous studies (Wang et al., 2011).

Dissolved gas sampling was also performed to investigate the variation of the dissolved CH_4 and CO_2 concentration in the water of the CW. The dissolved gas samples were collected and analyzed using the headspace air method as described by Ren et al. (2013). Water (30 ml) and argon gas (70 ml) were injected into a 100 ml preevacuated vial, and 1 ml $HgCl_2$ (20 mM) was added to inhibit microbial activity. The water was collected at the same time as the gas sampling. After a shaking (1 h), the vial was left at room temperature for 10 min. The headspace gas phase in the vial was collected for determining dissolved CH_4 and CO_2 concentration based on Henry' s Law and mass balance (Ren et al., 2013).

3. Results and discussion

3.1. Variations of environmental parameters and water quality

Fig. 2 shows the seasonal variation of the average air temperature and relative humidity from January 2014 to December 2014. There was an obvious seasonal variation for air temperature which was ranged from −10.1 °C to 36.5 °C in 2014. In addition, relative humidity during the experimental period varied significantly, and the average relative humidity was 54.8%, with the higher value in July (74.2%) and the lower value in January (35.6%). The variation of average water temperature in the CW, which ranged from 3.9 °C in Winter to 31.1 °C in Summer, was similar to air temperature during the experimental period, and the mean seasonal water temperature was slightly lower than the mean seasonal air temperature except for Winter (Table S1). Table 1 gives the effluent characteristics (the final effluent after the 7 FWS CW treatments) of the Wu River CW that were measured during the experimental period, and it showed that the final average effluent concentrations of COD, NH_4^+-N, NO_3^--N, NO_2^--N, TN and TP were 18.44 mg L^{-1}, 1.06 mg L^{-1}, 4.01 mg L^{-1}, 0.13 mg L^{-1}, 5.17 mg L^{-1} and 0.01 mg L^{-1}, respectively. The high oxygen level (DO > 10 mg L^{-1}) in the effluent indicates the predominance of aerobic conditions. On the whole, the main water quality parameters (i.e. COD, NH_4^+-N, pH and DO) can comply with the Grade III of Environmental Quality Standards for Surface Water (GB3838-2002) in China, which indicated a significant improvement in water quality of secondary effluents from a conventional WWTP by Wu River CW treatment. However, other parameters such as TN and TP could not meet the Grade III. In addition, there was seasonal fluctuation and in average removal performance of pollutants, which may be due to the seasonal variation of some important influencing factors such as macrophyte species and density, diversity of plants, loading rates and climatic condition (especially air temperature) during the whole experimental period (Brisson and Chazarenc, 2009; Vymazal, 2013b; Wu et al., 2011).

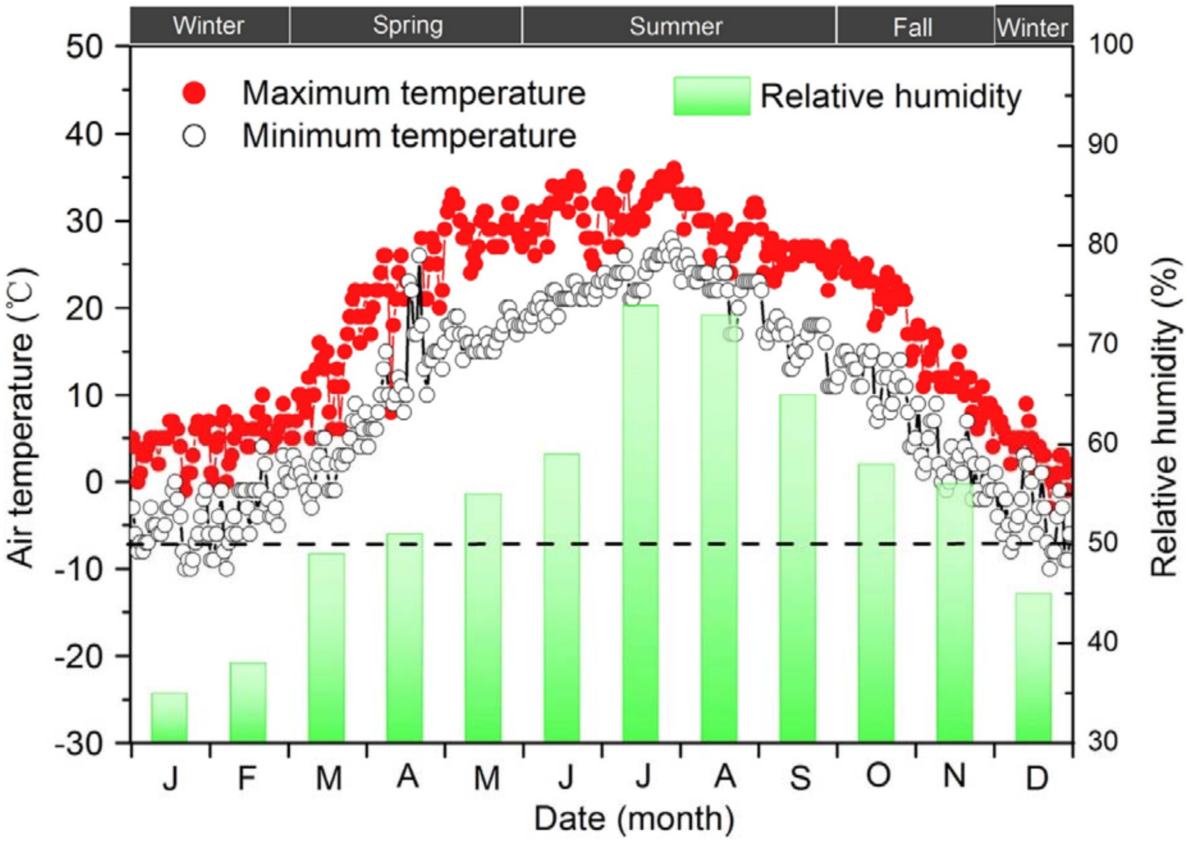


Fig. 2. Variation of air temperature and relative humidity during the experimental period.

3.2. Seasonal and spatial variations of organics removal

For organic pollutants removal, degradation aerobically and anaerobically is the classic removal routes in CW treatments. Aerobic degradation can be accomplished based on the available oxygen via atmospheric oxygen diffusion, convection (wind effect), and macrophyte root transfer into the plant rhizosphere, and anaerobic organics removal can proceed inside the sediment, lacking oxygen (Saeed and Sun, 2012). In this study, seasonal and spatial variations of COD removal in the Wu River CW over a period of one year (from January 2014 to December 2014) were evaluated, and the average concentrations of COD in the nine sites of the Wu River CW in different seasons are illustrated in Fig. 3. The data demonstrate a sustained and stable removal of organics from the secondary effluent of the municipal WWTP. However, average effluent concentrations of COD of the Wu River CW changed significantly with the different COD removal efficiency in different seasons of the one year. Furthermore, concentrations of COD varied considerably within each sampling site. In spring (March to May), the concentration of COD gradually decreased along the Wu River CW from 50.61 mg L^{-1} at the inlet to 20.69 mg L^{-1} in the outlet, indicating a removal efficiency of 59.11% (Fig. 3a). Concentrations of COD also varied considerably within each sampling location. A significant decrease was observed in the third sampling site (i.e. the first wetland unit), and then there was a slightly fluctuation along the CW. In summer (June to September), the similar dynamics of COD removal was obtained in the Wu River CW as those observed during the spring season. COD concentrations of the effluent was 16.53 mg L^{-1} which resulting a higher removal efficiency of 65.98% (Fig. 3b). However, a significant decrease in the concentration of COD, reaching 15.57 mg L^{-1}, was observed in the fourth sampling site (i.e. the second wetland unit), and then the value of COD concentration increased weakly with the stable variation in the following sampling sites of the CW. But these differences were not statistically significant. It was found that CW system also showed better COD removal effects in autumn (October to November), and the effluent concentration was 15.54 mg L^{-1} which indicating a removal efficiency of 63.86%. Even if the air temperature in this season began decrease, COD concentrations in the different sampling sites except inflow site were all stabilized at the range of 8.72–22.12 mg L^{-1} (Fig. 3c), especially in the seventh sampling site (nearly the fifth wetland unit) with lowest COD concentration. During the coldest season (i.e. December, January and February), COD concentration in different sampling sites had a distinct fluctuating trend of early gradual decrease and later sudden increase along the CW (Fig. 3d). Unlike in the warm months, a significant increase in the concentration of COD, reaching 29.22 mg L^{-1}, was observed in the sixth wetland unit. Then, the effluent COD concentration stabilized at 21.22 mg L^{-1}, which basically meets the Grade III of Environmental Quality Standards for Surface Water (GB3838-2002) in China.

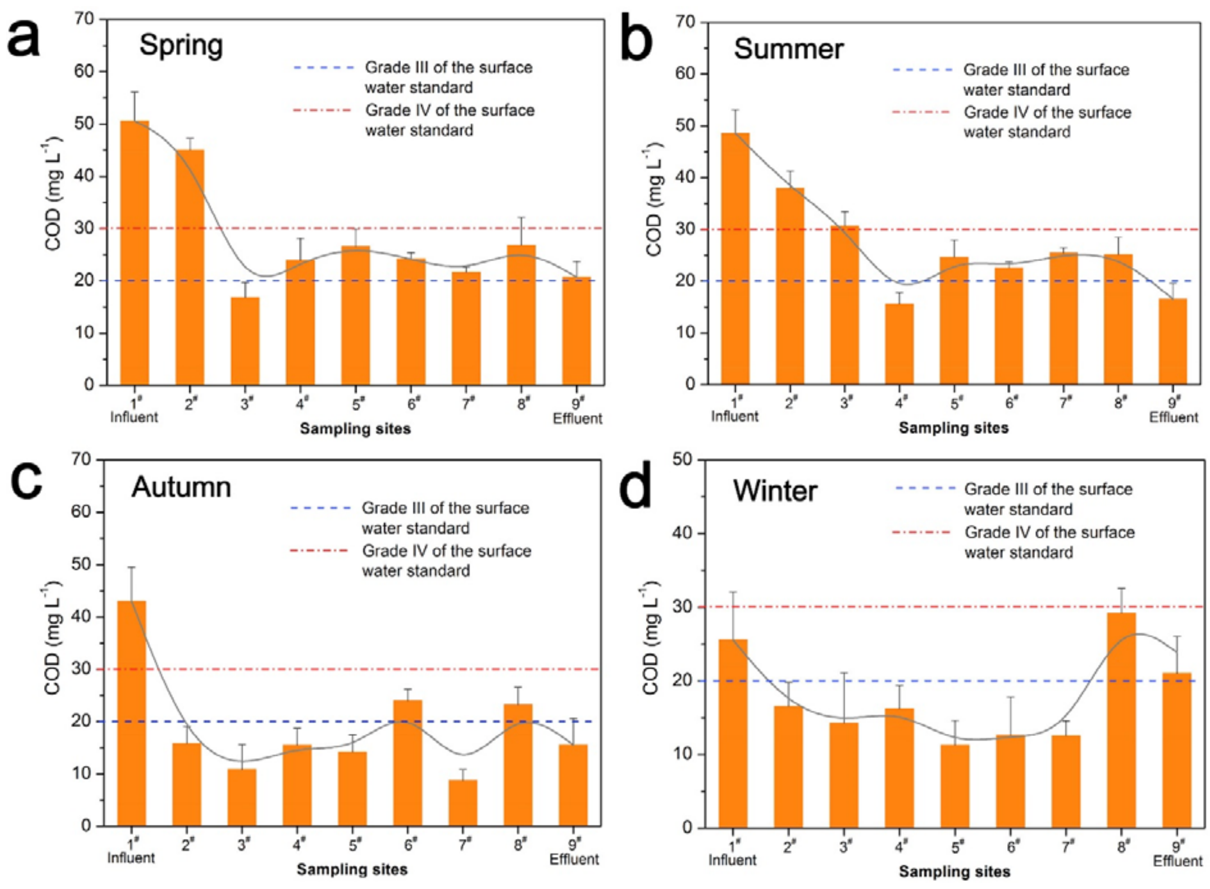


Fig. 3. Seasonal and spatial variation of COD concentrations in the Wu River multi-stage constructed wetland.

On the whole, results in this study showed that significant seasonal influences on organics removal were presented in the wetland system, and the mean removal efficiencies were obvious pronounced in spring, summer and autumn compared to winter. Moreover, there were obvious spatial variations in seasonal organics removal effects. Organics in CWs can mainly be degraded by both aerobic and anaerobic microbial processes as well as by sedimentation and filtration of particulate organic compounds (Saeed and Sun, 2012). Organics removal processes in FWS CWs may be generally influenced by the different environmental parameters and operational conditions such as: temperature, loading rate, retention time, vegetation and harvesting (Wu et al., 2011, 2014; Saeed and Sun, 2012). Particularly in order to investigate whether the efficiency of organics removal of the multi-stage CW was impacted by seasonal variations in temperature and loading rate, COD removal by the CW observed for each season was compared to average seasonal air temperatures and inflow COD loading rates. Fig. 4 presents the effect of seasonal variations in air temperature and inflow COD loading rate on the rate of COD removal in the CW. Linear relationship between air temperature and COD removal rate during different seasons was found to be significant ($R^2 = 0.98$, $p < 0.01$). As is shown in Fig. 4a, COD removal rate increased significantly with the air temperature rising from 2 °C (Winter) to 18 °C (Spring), but there was less significant variation in COD removal rate when air temperature was between 18 °C (Spring) and 33 °C (Summer). This suggested that a proper air temperature range for COD removal was around 18–33 °C under certain conditions. The possible explanation might be that organics removal mechanisms in CWs was mainly microbial processes by microbial community, and microbial activity could be directly affected by water temperature which was caused by air temperature variation (Saeed and Sun, 2012; Lv et al., 2017). On the other hand, air temperature could significantly affect the growth and establishment of wetlands plants which in turn influenced water purification (Rai et al., 2013; Meng et al., 2014). In the CW, wetland plants and microbes grow well in warm season, but during the winter season, plant litter was decomposed resulting in the release of organic matter into water. Moreover, the diversity of different macrophyte types in different treatment units would cause significant spatial dynamics of microbial community in CWs (Button et al., 2016; Lv et al., 2017). The influence of evapotranspiration should also be considered. In this study, it is estimated that evapotranspiration from different CW cells was high in summer (approximately 8 mm d^{-1}), and evaporation values in CW cells with more vegetation were higher than that in CW cells with more open water area. Evapotranspiration might have a negative effect on COD removal rates because it reduces the amount of water and increases the concentration of pollutants (Białowiec et al., 2014). As is shown in Fig. 4b, significant line relationship between COD loading rate and COD removal rate was also observed ($R^2 = 0.99$, $p < 0.01$), which indicated a positive correlation among the influent wastewater quality and organics removal. It can be observed that the wastewater discharged into the river was significantly more contaminated during spring, summer and fall than in winter, and COD removal rate in CWs rose clearly with the increase of loading rate of influent wastewater. These results are consistent with previous research which reported that increase of organic loading often coincided with greater organics removal rate (Sun and Saeed, 2009; Saeed and Sun, 2011). However, excessive loading rates would cause accumulation of organic matter and lower removal efficiencies in CWs (Landry et al., 2007). For polishing secondary effluent of the WWTP in this study, the inflow COD loading rate of 1.8–2.0 g m^{-2} d^{-1} could be appropriate for achieving the higher organics removal efficiency in the multi-stage CW. But it should be noted that it was difficult to identify an optimal loading rate that corresponded to the highest organics removal efficiency in CWs under complicated conditions.

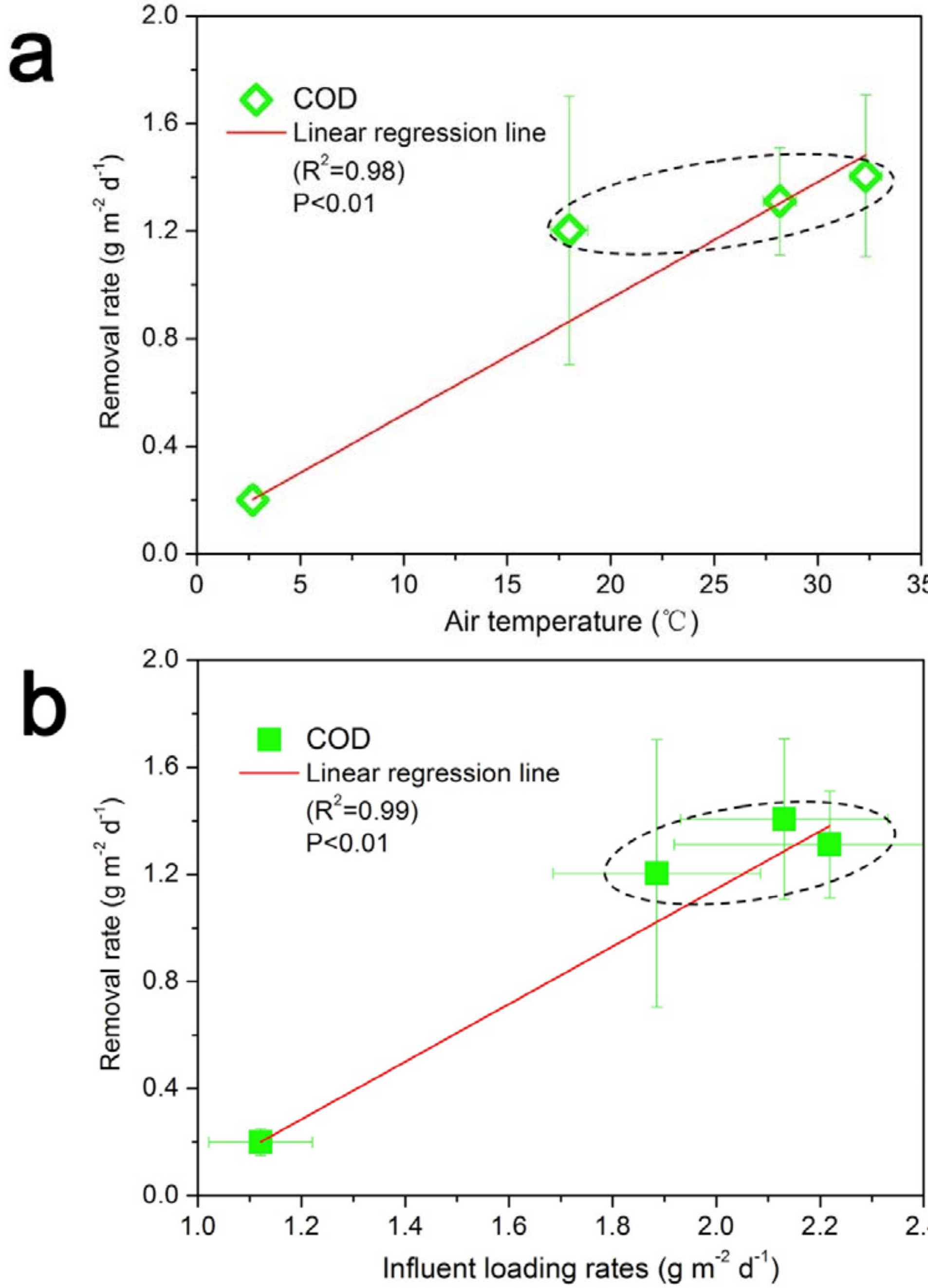


Fig. 4. Effect of seasonal variations in temperature (a) and inflow loading rate (b) on the rate of organics removal in the Wu River multi-stage constructed wetland. R^2 represents the coefficient of determination of the linear model between seasonal temperature (inflow loading rate) and organics removal.

3.3. Seasonal and spatial variations of CH_4 emission

In order to understand the carbon dynamics in a large-scale CW system for the maximum environmental benefit, a measurement of seasonal and spatial CH_4 emissions from the Wu River CW over a period of one year were conducted. Fig. 5 presents the average emissions of CH_4 from the CW in different seasons throughout the long-term field study. There was significant seasonal variation in CH_4 emission, with the average CH_4 flux varying from 3.78 mg m^{-2} d^{-1} to

35.54 mg m^{-2} d^{-1}. The higher flux of CH_4 was observed in spring compared to summer (Fig. 5a and b), and a lower CH_4 flux occurred in fall and winter (Fig. 5c and d). On the whole, the average CH_4 fluxes in spring and summer were 5–10 times higher than that in fall and winter. Average CH_4 emission fluxes also had obvious spatial variations in different sampling sites of the CW. Specially in spring, summer and fall, and there was strong evidence of CH_4 fluxes in the middle sites of the CW being significantly increased compared to inflow and outflow sites. However, the insignificant spatial variation of CH_4 fluxes was found in winter when the CW became a weak source of CH_4. It should be noted that when CH_4 emissions were high, the variation in the emission rates was also greatest. Both the minimum and maximum CH_4 emission fluxes were measured in warm seasons. Particularly, an obvious uptake of CH_4 was found in the outflow site in summer and winter, which indicating a net CH_4 sink. The above results suggested that seasons might have a remarkable effect on spatial variation of CH_4 emissions in the Wu River CW. The corresponding seasonal and spatial change of dissolved CH_4 concentrations was also observed with the variation of the CH_4 fluxes. In spring, the dissolved CH_4 concentration measured in the Wu River CW was gradually increasing along the CW from 0.02 mg L^{-1} in the inlet to 0.04 mg L^{-1} in the outlet (Fig. 5a). But compared with the variation in the spring season, the different dynamics of dissolved CH_4 concentration in the Wu River CW was detected in summer, fall and winter, which showed a variation trend of a significant decrease in the initial sampling sites with a significant increase later, and then a suddenly drop at the outflow sampling location.

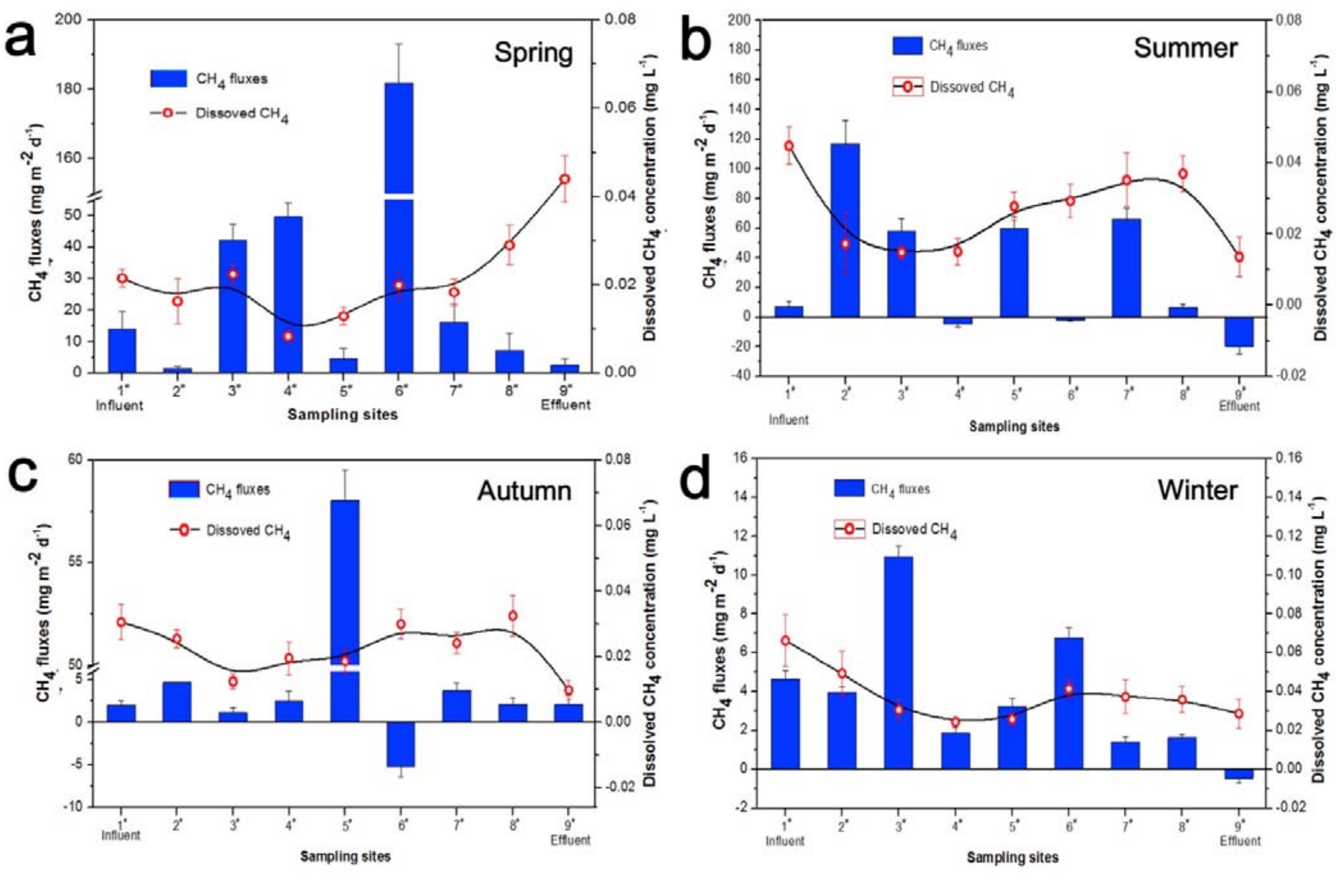
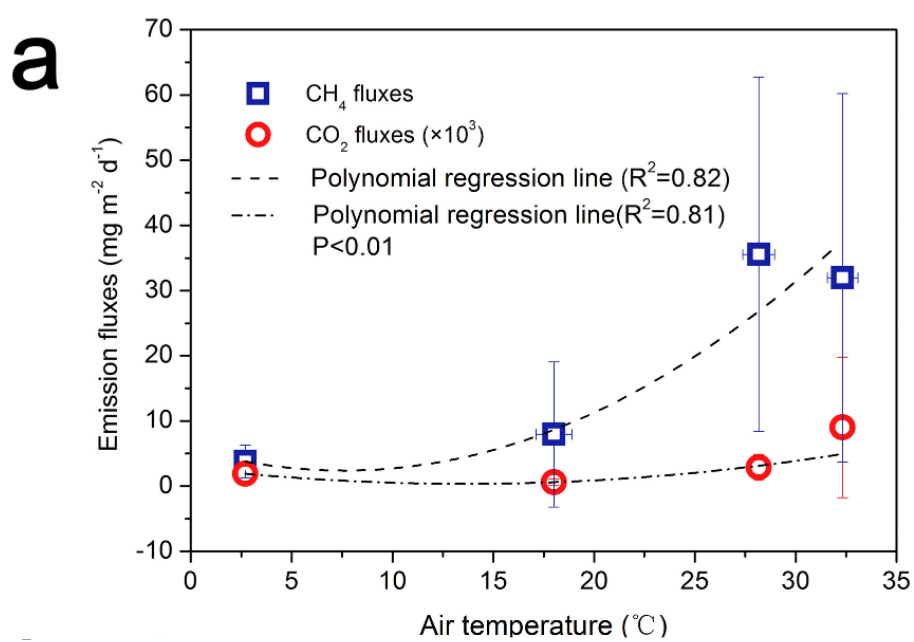


Fig. 5. Seasonal and spatial CH_4 fluxes and dissolved CH_4 concentrations in the Wu River multi-stage constructed wetland.

GHG emission from CWs can generally be influenced by various environmental conditions and operating parameters such as DO, HRT, water depth, available organic carbon, temperature and vegetation (Wu et al., 2017; Mander et al., 2014). The results in this study also indicated that the CH_4 emission from the CW could be affected by air temperature which represented seasonal water temperature directly. Fig. 6a shows the polynomial regression relationship between CH_4 fluxes and air temperature ($R^2 = 0.82$, $p < 0.01$). It seemed that the rate of CH_4 flux from CW increased with the rise of air temperature, and this is in agreement with findings from earlier studies which indicated that temperature is positively correlated with greenhouse gas emissions in CWs (Maucieri et al., 2017). The possible reason may be that microbial activity in wetlands generally increases at a proper temperature (Mander et al., 2014). Temperature can also affect vegetation productivity, cover, and biomass, which will then influence CH_4 emission by transporting CH_4 to the atmosphere through plant tissues directly (Mitsch et al., 2013; Murray et al., 2017). On the other hand, it is well recognized that temperature affects directly plant photosynthesis and evapotranspiration, and thus increases gas transportation, which would give a positive effect on CH_4 emission (Zhao et al., 2016). Pangala et al. (2010) investigated the response of CH_4 emissions to temperature in CWs, and showed that CH_4 emissions from CWs increased exponentially and significantly with water temperature from 10 °C to 30 °C. CH_4 emission may be influenced by other factors such as influent pollutants concentrations (Wang et al., 2008). Our results also indicated that influent COD loading rate significantly influence CH_4 emission (Fig. 6b). As is shown in Fig. 6b, a positive correlation between inflow loading rate and CH_4 emission rate was observed ($R^2 = 0.97$, $p < 0.01$). These results are in agreement with findings from earlier studies which indicated that a significant correlation between the inflow organics loading and CH_4 emission values in CWs based on the multiple regression analysis (Mander et al., 2014). However, it should be noted that there was some limit level for CH_4 emission at a certain loading rates. The possible reason is that the rate of methanogenesis might be inhibited by increased concentration of ammonia or accumulation of volatile fatty acids (Mata-Alvarez et al., 2000; Wang et al., 2008). On the whole, for the multi-stage CW polishing secondary effluent of the WWTP in this study, the inflow COD loading rate of 1.8–2.0 g m^{-2} d^{-1} could be appropriate for minimizing CH_4 emission with a higher organic removal efficiency.



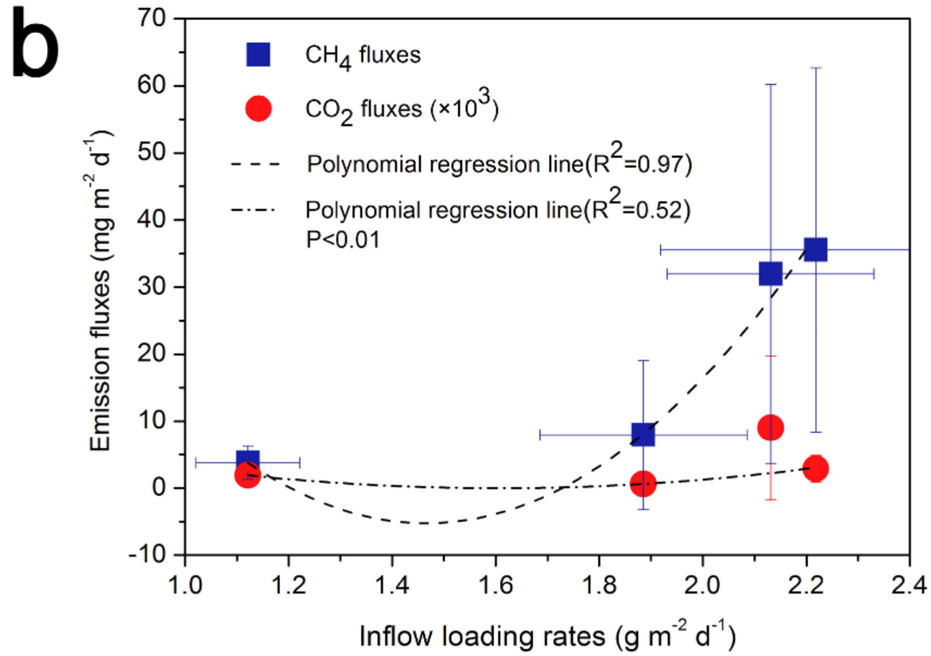


Fig. 6. Effect of seasonal variations in temperature (a) and inflow loading rate (b) on emission fluxes of CH_4 and CO_2 from the Wu River multi-stage constructed wetland. R^2 represents the coefficient of determination of the polynomial model between seasonal temperature (inflow loading rate) and emission of CH_4 and CO_2.

3.4. Seasonal and spatial variations of CO_2 emission

Although CO_2 is a major GHG, there are only few studies reporting on CO_2 emission in CWs (Mander et al., 2014; Wu et al., 2017). Therefore, the CO_2 emissions from different sites of the Wu River CW were also measured in this study for understanding the variation of CO_2 emission in the large-scale CW system for the treatment of secondary effluent. As shown in Fig. 7, the emission rates of CO_2 from the CW were significant different in different seasons during the one year. The average CO_2 emission rates were higher in spring (2889.41 mg m^{-2} d^{-1}) and summer (8992.71 mg m^{-2} d^{-1}), but lower in autumn (610.78 mg m^{-2} d^{-1}) and winter (1908.35 mg m^{-2} d^{-1}). The average CO_2 fluxes in spring and summer were 2–15 times higher than that in fall and winter. The significant spatial variation in the average CO_2 emission rates was also found in different sampling sites of the CW. It is indicated that the variation in the flux rates was greatest when CO_2 emissions were high. Both the minimum and maximum CO_2 fluxes were measured in summer with the CO_2 flux varying from −1019.72 mg m^{-2} d^{-1} to 42549.78 mg m^{-2} d^{-1}. In addition, strong CO_2 emission occurred in the front and rear sites of the CW while negative CO_2 emission was found in the middle sites. The evident spatial variation of CO_2 fluxes was also found in spring, fall and winter, however, the negative CO_2 emission was only observed at the outflow site. These results can be explained by the previous research that plant autotrophic respiration and plant photosynthesis increased with high biomass production, which may result a higher net exchange of CO_2 between CWs and the atmosphere (Mander and Teiter, 2005; Mander et al., 2014). In addition, it is clearly reported that the significant role of wetland plants, which bring a large quantity of atmospheric CO_2 into the CW, thereby showing the small net GHG sink (Mitsch et al., 2013). The corresponding seasonal and spatial change of dissolved CO_2 concentrations was also observed with the variation of the CO_2 fluxes (Fig. 7). In spring, the dissolved CO_2 concentration measured in the Wu River CW was significantly increasing along the CW from 0.12 g L^{-1} in the inlet to 0.74 g L^{-1} in the middle sites, and then decreased to 0.11 g L^{-1} in the outlet (Fig. 7a). However, the different dynamics of dissolved CO_2 concentration in the Wu River CW was detected in summer, fall and winter, which showed a variation trend of a gradual decrease from the initial sampling sites to the outflow sampling location.

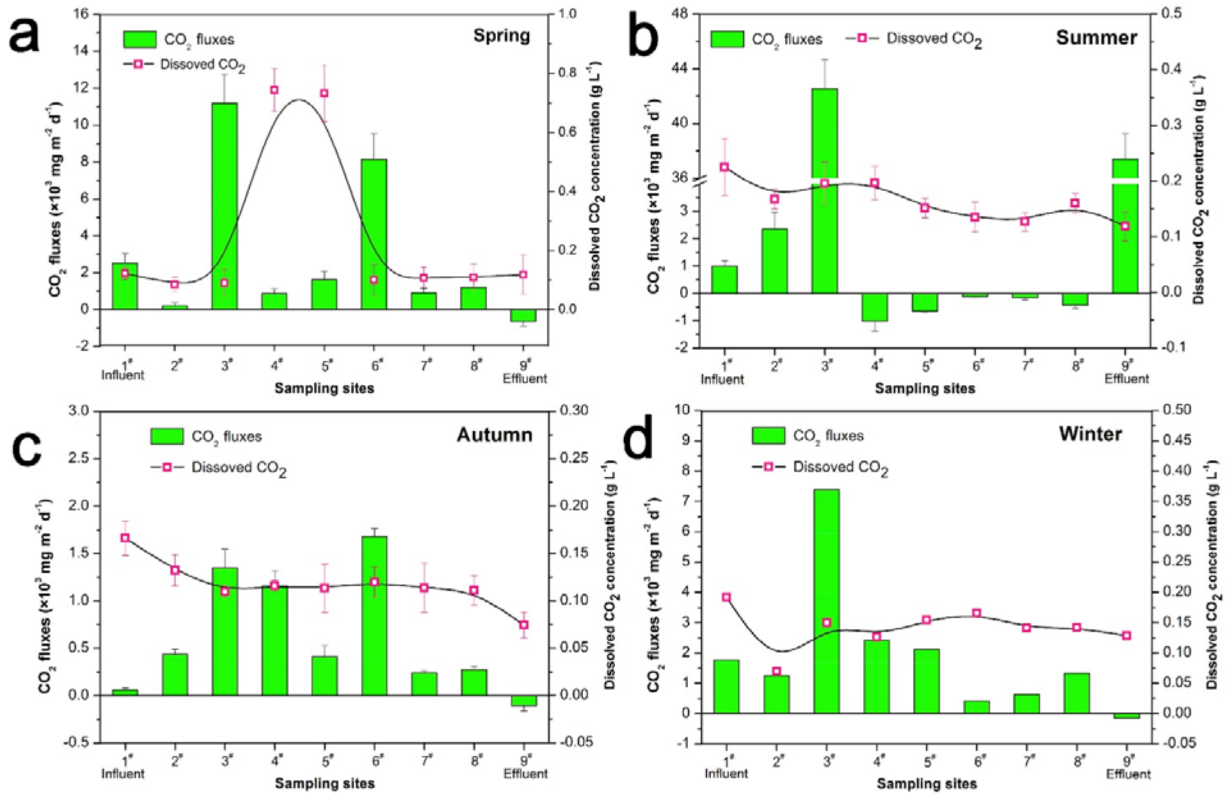


Fig. 7. Seasonal and spatial CO_2 fluxes and dissolved CO_2 concentrations in the Wu River multi-stage constructed wetland.

To investigate whether the CO_2 emission of the CW was impacted by seasonal variations in temperature and inflow loading rates, the average CO_2 emission in the CW observed for different seasons was compared to average seasonal air temperatures and inflow COD loading rates. As indicated in Fig. 6a, the polynomial regression relationship between air temperature and CO_2 emission rates revealed that CO_2 emission rate was associated with seasonal air temperature ($R^2 = 0.81$, $p < 0.01$). A slight increase in rate of CO_2 emission from the CW was presented under high temperature conditions. The possible reason may be that microbial activity for organic degradation in CWs generally increases at a proper climatic condition (such as temperature) (Mander et al., 2014). In addition, temperature affects directly plant photosynthesis and respiration as well as evaporation, which influences directly CO_2 emission (Mitsch et al., 2013). This is in agreement with the previous results which reported that the CO_2 flux from the wetlands might be affected by the seasonal temperature variation (Mander and Teiter, 2005), and Trumbore et al. (1996) indicated that temperature had a strong influence on soil carbon dynamics regulating CO_2 uptake or emission to the atmosphere. A positive correlation between average air temperature and CO_2 emission in the CWs was also confirmed by Maucieri et al. (2014). But there was an evident difference in the importance of temperature in CO_2 emissions from different designed or operated

CWs in diverse climate sites (Wu et al., 2016a,b). Hence, the relationship between CO_2 emissions and influent COD loading rates in the large-scale CW system in different seasons was assessed, but as shown in Fig. 6b, an insignificant correlation was observed between inflow loading rate and CO_2 emission rate (R^2 = 0.52, $p < 0.01$). This appears to be due to an obscure interaction between CO_2 fluxes and organic loading rates when it is at low loading conditions, although the characteristics (i.e. biodegradability and loading) of the organic matter was the key factor in influencing the intensity of organics removal processes in CWs (Saeed and Sun, 2012; Mander et al., 2014). Generally, for the multi-stage CW polishing secondary effluent of the WWTP, the proper inflow COD loading rate for a low CO_2 emission and high organics removal efficiency is uncertain and worthy of further long-term investigation. On the other hand, it should also be noted that a comprehensive analysis of the environmental and ecological benefit would be required for the CW as a water purification technology when considering the aspect of the CW sustainability. Specifically, the potential contribution of GHG (CH_4 and CO_2) emission from the CW may reduce the environmental and ecological benefits although an excellent organic removal performance was achieved in this study. Therefore, a feasible method or management for mitigating GHG emissions in CWs should be paid special attention.

4. Conclusions

The long-term investigation of the large-scale multi-stage CW for polishing domestic WWTP effluents was performed in northern China, and the results indicated that water quality of Wu River CW could comply with the Grade III of Environmental Quality Standards for Surface Water in China. However, Wu River CW might be a potential emission source of CH_4 (3.78–35.54 mg m^{-2} d^{-1}) and CO_2 (610.78–8992.71 mg m^{-2} d^{-1}). Significant seasonal variations of organics removal and emission of CH_4 and CO_2 were observed in the Wu River CW with a higher COD removal efficiency in summer and fall and higher CH_4 and CO_2 emission rate in spring and summer. The rates of COD removal and CH_4 emission increased significantly with the rise of air temperature and inflow COD loading rates, but CO_2 emission rate was observed to be insignificantly associated with air temperature and inflow COD loading rates. Our results will be helpful for understanding the dynamics and cycles of carbon in large-scale multi-stage CWs, and further field experiments will be required to optimize the design, operation and management of multi-stage CW treatments and its environmental sustainability.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.envpol.2017.09.048.

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