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Treatment of oil and grease in produced water by a pilot-scale constructed wetland system using biogeochemical processes

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HIGHLIGHTS

- A pilot-scale wetland treatment system was designed and constructed.
- Sequential reducing and oxidizing cells promoted specific biogeochemical processes.
- Metals and oil in simulated oilfield produced water were treated effectively.
- Biogeochemical conditions changed with mass loading of oil, affecting treatment.
- An oil–water separator decreased inflow concentrations of oil.

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ABSTRACT

Constructed wetland treatment systems (CWTSs) can effectively remove many constituents that limit beneficial use of oilfield produced water. The objectives of this investigation were: (1) to assess the effect of mass loadings of oil and grease (O & G) on treatment performance in pilot-scale subsurface flow and free water surface CWTS series having sequential reducing and oxidizing cells, and (2) to evaluate effects on treatment performance of adding a pilot-scale oil–water separator. Increase in O & G mass loading from 5 to 20 mg min^{-1} caused decreases in both dissolved oxygen concentration and sediment redox potential, which affected treatment performance. Biogeochemical pathways for removal of O & G, iron, and manganese operate under oxidizing conditions, and removal rate coefficients for these constituents decreased (0.905–0.514 d^{-1} for O & G, 0.773–0.452 d^{-1} for iron, and 0.970–0.518 d^{-1} for manganese) because greater mass loading of O & G promoted reducing conditions. With increased mass loading, removal rate coefficients for nickel and zinc increased from 0.074 to 0.565 d^{-1} and from 0.196 to 1.08 d^{-1}, respectively. Although the sequential reducing and oxidizing cells in the CWTS were very effective in treating the targeted constituents, an oil–water separator was added prior to wetland cells to enhance O & G removal at high inflow concentration (100 mg L^{-1}). The oil–water separator removed approximately 50% of the O & G, and removal extents and efficiencies approximated those observed at 50 mg L^{-1} inflow concentration during treatment without an oil–water separator.

1. Introduction

Oilfield produced water is defined as water brought to the surface as a result of oil production (Veil et al., 2004). Twenty-one billion barrels of produced water were generated in 2007 by onshore and offshore facilities with 87% from oil production activities (Clark and Veil, 2009). Common naturally occurring constituents of concern that limit the use of produced water include organic compounds, anions, cations, nitrogen compounds (nitrate, nitrite, and ammonia), total dissolved solids, and total suspended solids (Veil et al., 2004; Benko and Drewes, 2008). Simulated oilfield produced water used for this experiment was based on the composition of a produced water originating from an oilfield located in sub-Saharan Africa that contains oil and grease (O & G), Fe, Mn, Ni, and Zn as constituents of concern (Horner et al., 2011a).

Strategies to manage produced water include underground injection, surface discharge, and beneficial use (Veil et al., 2004; Benko and Drewes, 2008). Beneficial use (e.g. livestock watering, irrigation, power plants, aquaculture, wildlife habitat, aquifer recharge) of produced water is attractive in regions where water demand surpasses water supply and can become an option when constituents of concern can be treated to acceptable levels (Veil

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et al., 2004). Constructed wetland treatment systems (CWTSs) are a potential treatment method for produced water. CWTSs have been utilized to treat a variety of waters including wastewater originating from farming practices, acid mine drainage, petroleum refinery effluents, flue gas desulfurization wastewater, brackish oilfield produced water, and other industrial effluents (Cronk, 1996; Barton and Karathanasis, 1998; Knight et al., 1999; Gillespie et al., 2000; Mooney and Murray-Gulde, 2008; Murray-Gulde et al., 2008). CWTSs are robust in nature, have the capacity to treat numerous constituents simultaneously, and have low associated costs (Mooney and Murray-Gulde, 2008; Rodgers and Castle, 2008). Contaminants can be targeted for removal through biogeochemical processes (transfers or transformations) by manipulating environmental conditions of the CWTS, soil type, and the types of plants (Rodgers and Castle, 2008). Flow patterns in CWTSs include subsurface flow (SSF; water level maintained below surface of the hydrosoil) and free water surface (FWS; water level maintained above hydrosoil). Previous research (Horner et al., 2011b) showed that pilot-scale CWTSs can effectively treat O & G at inflow concentrations up to 50 mg L^{-1} (2.3–5.2 mg min^{-1} mass loading). Because CWTSs could be exposed to greater O & G loadings, data on treatment performance at increased loads of O & G are needed. The purpose of this investigation was to evaluate a specifically designed pilot-scale CWTS for treating oilfield produced water with 100 mg L^{-1} O & G concentration (mass loading $\geqslant$5 mg min^{-1}). An oil–water separator, a passive device using gravity separation based on density differences between oil and water, was incorporated in the system. Oil collected from an oil–water separator has potential to be sold, which could help alleviate costs associated with produced water treatment. Specific objectives of this investigation were: (1) to assess effects of O & G mass loadings on treatment performance in pilot-scale SSF and FWS series, and (2) to evaluate treatment performance of a pilot-scale SSF series containing an oil–water separator.

2. Materials and methods

2.1. Pilot-scale constructed wetland treatment system

A pilot-scale CWTS, which was designed and constructed in a climate-controlled greenhouse located in Clemson, SC (USA), was used to assess treatment performance for oilfield produced water. The pilot-scale system was designed based on biogeochemical pathways to decrease aqueous concentrations of targeted constituents of concern (O & G, Fe, Mn, Ni, Zn) in simulated produced water. Use of simulated produced water reduces transportation costs associated with using actual produced water and allows precise control of water composition. Simulated produced water was formulated by addition of Shell Rotella T® motor oil and high purity salts ($FeCl_3$, $MnCl_2{\cdot}4H_2O$, $NiCl_2{\cdot}6H_2O$, and $ZnCl_2$; Fisher Scientific Inc., Fair Lawn, NJ) to a 3785-L polypropylene carboy retention basin containing municipal water. Additional salts ($NaHCO_3$, $MgSO_4{\cdot}7H_2O$, KNO_3, and $CaCO_3$) were added to simulate hardness, pH, and ionic composition of the produced water. The simulated produced water was formulated based on composition of a specific oilfield produced water studied by Horner et al. (2011a). The simulated produced water flowed from the retention basin to the first cell of each of three treatment series via Fluid Metering Inc. (FMI®) piston pumps operating at a flow rate that maintained the targeted hydraulic retention time (HRT).

The CWTS was designed for sequential reducing and oxidizing cells, with the mass loading of oil and grease to the CWTS providing organics to promote reducing conditions. Three series were constructed (2 SSF = series A and B, and 1 FWS = series C), each consisting of four wetland cells (Supplementary Figs. S1, S2). Series A and B were identical except that series A included an oil–water separator, described in Section 2.3. Each cell was contained within a 378-L Rubbermaid® utility tank, 123-cm long by 64-cm wide by 61-cm deep. Hydrosoil in the SSF cells, which utilized vertical flow, was composed of 20 cm of pea gravel (5–10 mm in diameter) overlain by 40 cm of medium-sized, granitic gravel (20–30 mm diameter). SSF cells were planted with *Phragmites australis* (common reed), a macrophyte native to Sub-Saharan Africa and found throughout temperate and tropical regions. Cells in the FWS series were filled to a depth of 36 cm with hydrosoil composed of coarse, well-sorted, quartz sand obtained from 18-Mile Creek near Clemson, SC. The first cell in the FWS series was planted with *Schoenoplectus californicus* (bulrush). The second, third, and fourth cells of the FWS series were planted with *Typha latifolia* (cattail).

2.2. O & G mass loading and treatment performance

The effect of O & G mass loading on treatment performance of CWTS series B and C was investigated by changing O & G inflow concentration and HRT. O & G was loaded at 50 mg L^{-1} targeted inflow concentration at a rate providing a nominal 4 d HRT (24 h for each wetland cell) from August–October 2010, 100 mg L^{-1} O & G with a 4 d HRT from October–November 2010 and February–March 2011, and 100 mg L^{-1} O & G with a 2 d HRT (12 h for each wetland cell) from March–April 2011. Nominal O & G mass loadings were 5 mg min^{-1} at 50 mg L^{-1} inflow concentration and 4 d HRT, 10 mg min^{-1} at 100 mg L^{-1} inflow concentration and 4 d HRT, and 20 mg min^{-1} at 100 mg L^{-1} inflow concentration and 2 d HRT.

To determine effects of the O & G loadings on hydrosoil conditions, oxidation–reduction (redox) potential was measured using platinum-tipped redox probes in the hydrosoil of each cell. Probes remained *in situ* for the duration of experiments. Redox measurements were made with an Accumet® calomel reference electrode using a Fluke® 77 voltage meter (Faulkner et al., 1989). Hydrosoil redox potential was measured in September 2010, October 2010, November 2010, March 2011, and April 2011.

General water chemistry parameters (alkalinity, hardness, pH, and dissolved oxygen) were measured in aqueous samples collected in 50 mL centrifuge tubes from series inflow and from outflow of each cell. Dissolved oxygen concentration and pH were measured using direct instrumentation, and alkalinity and hardness were measured in accordance with standard methods (APHA, 2005). Temperature and conductivity of outflow water from the cells also were measured.

To determine the ability of each series to decrease concentrations of O & G, aqueous samples for measurement of O & G concentration were collected in 1L glass jars with Teflon® lined lids from the series inflow and from cell outflows. EPA method 1664 (USEPA, 1999), a gravimetric method involving n-hexane extraction, was used for O & G analyses.

Aqueous samples for measurement of Fe, Mn, Ni, and Zn concentrations were collected in 50-mL centrifuge tubes from series inflow and from outflow of each wetland cell to determine the ability of each series to decrease concentrations of metals. Metal analyses were performed according to EPA method 200.7 (USEPA, 1994) using inductively coupled plasma-atomic emission spectrometry (ICP-AES; SPECTROFLAME-EOP, Spectro Analytical Instruments, Kleve, Germany). Due to instrument interferences from O & G concentrations, samples containing >50 mg L^{-1} O & G concentration were diluted before analysis using ICP-AES.

O & G concentrations were measured in motor oil standards (i.e. known mass of motor oil in a known volume of water). For every tenth sample analyzed, O & G concentration in a matrix spike was measured by collecting duplicate samples, adding 20 mg motor oil to one of the samples, and analyzing both samples. Percent recoveries within 78–114% for standards and matrix spikes were acceptable (USEPA, 1999). Standard recoveries were measured with a prepared blank and Fe, Mn, Ni, and Zn standards; standard additions were measured for every tenth sample (USEPA, 1994). Analyses were considered acceptable if standard recoveries were within ±10% of calibration concentrations for individual metals and standard addition percent recoveries were between 70% and 130% (USEPA, 1994).

Removal rate coefficients were calculated for O & G and metals to determine the effectiveness of each design. Removal rate coefficients (k) were calculated assuming first-order rate kinetics (Rousseau et al., 2004; Crites et al., 2006).

$$\text{Removal rate coefficient } (k) = \frac{-\ln([C]/[C_o])}{t} \quad (1)$$

where $[C_o]$ is the initial inflow concentration (mg L^{-1}), $[C]$ is the series outflow concentration (mg L^{-1}), and t is the time (days) corresponding to HRT of the series. Removal efficiencies, defined as the percent decrease in outflow concentration relative to inflow concentration, were calculated for O & G and metals using the following equation.

$$\text{Removal efficiency}(\%) = \frac{[C_o - [C]}{[C_o]} \times 100 \quad (2)$$

where $[C_o]$ is the initial inflow concentration (mg L^{-1}) and $[C]$ is the outflow concentration (mg L^{-1}). Removal extent is defined as the series outflow concentration, and can also be used to evaluate treatment performance of the system.

2.3. Effect of oil–water separator on treatment performance

An oil–water separator was included in SSF series A to investigate its effect on treatment of O & G at a nominal mass loading of 10 mg min^{-1}. To achieve this mass loading, the inflow concentration of O & G was 100 mg L^{-1} and HRT was 4 d. The oil–water separator was the initial treatment step in this series, with the oil–water separator installed between the retention basin and the first wetland cell. Construction of the oil–water separator was based on an American Petroleum Institute design (API, 1990) and targeted the oil fraction that can be physically separated by the difference in specific gravities of oil and water. Dimensions of the oil–water separator were 122 cm long by 61 cm wide by 33 cm deep. Oil removal techniques implemented by the oil–water separator included baffles and filtration (Wilkinson et al., 2000). Filtration was achieved through insertion of Fairfield® Poly-fil in one of the compartments of the oil–water separator. Series A was sampled at the inflow and outflow of the oil–water separator and at the outflow of each cell. General water chemistry parameters and O & G concentrations were measured using the analytical methods described above. Removal rate coefficients and removal efficiencies for O & G were calculated using Eqs. (1) and (2), respectively.

3. Results

3.1. Effect of O & G mass loading on treatment performance

3.1.1. Hydrosoil conditions and general water chemistry

For both the SSF and FWS series, hydrosoil conditions became more reducing as O & G mass loading increased (Table 1; Supplementary Fig. S3). Mean redox potential in the first three cells decreased from 80 to 23 mV for the SSF series and from 63 to 20 mV for the FWS series as O & G mass loading increased from ~5 to 10 mg min^{-1}. Redox potential decreased by an average of 67 mV for SSF cells and 82 mV for FWS cells as mass loading increased from ~10 to 20 mg min^{-1}. The greatest change in redox potential as mass loading increased from ~10 to 20 mg min^{-1} occurred in the first cells (decrease of 166 mV for SSF and 157 mV for FWS) and the least change occurred in the final cells (decrease of 11 mV for both SSF and FWS). Oxidizing conditions (>−50 mV; Rodgers and Castle, 2008) were maintained in the final cell of both series for all O & G loadings.

The amount of change in dissolved oxygen concentration from inflow to outflow increased as O & G mass loading increased. For O & G mass loadings of ~5, 10, and 20 mg min^{-1}, mean decrease in dissolved oxygen concentration from inflow to outflow was 1.02, 1.87, and 3.45 mg L^{-1}, respectively, for the SSF series and 1.17, 1.73, and 2.94 mg L^{-1}, respectively, for the FWS series. Mean dissolved oxygen concentration for all mass loadings was greater in outflow from the first cell (6.46 mg L^{-1} for SSF and 6.58 mg L^{-1} for FWS) than in outflow from the final cell (5.86 mg L^{-1} for SSF and 6.01 mg L^{-1} for FWS).

In wetland cells of both series, measured conductivity of the water ranged from 162 to 265 μS cm^{-1}, pH from 6.09 to 7.24, temperature from 21.7 to 28.1 °C, alkalinity from 25 to 75 mg L^{-1} as $CaCO_3$, and hardness from 21 to 62 mg L^{-1} as $CaCO_3$.

3.1.2. Treatment of O & G

Outflow concentration (removal extent) of O & G was greater, removal rate coefficient was less, and removal efficiency was less at ~10 mg min^{-1} O & G mass loading than at ~5 mg min^{-1} mass loading for both the SSF and FWS series (Tables 1 and 2; Supplementary Fig. S4). Removal efficiency for both series ranged from 85.3% to 94.4% ($n = 8$) at ~10 mg min^{-1} loading compared to 97.2–97.3% ($n = 4$) at ~5 mg min^{-1} loading. For both series, removal extent was greater and removal efficiency was less at ~20 mg min^{-1} mass loading than at ~10 mg min^{-1} mass loading. At a mass loading of ~20 mg min^{-1}, removal efficiency ranged from 68.4% to 70.2% ($n = 2$) for the SSF series and from 64.2 to 71.2% ($n = 2$) for the FWS series.

3.1.3. Treatment of metals

For both the SSF and FWS series, with an increase in O & G mass loading from ~5 to 10 mg min^{-1}, outflow concentrations increased for Fe and Mn and decreased for Ni and Zn (Table 3; Supplementary Fig. S5). In the SSF series, removal efficiency decreased for Mn and increased for Fe, Ni, and Zn (Table 4). With the increase in O & G loading from ~5 to 10 mg min^{-1} to the FWS series, removal efficiency for Fe and Mn decreased and removal efficiency for Ni and Zn increased.

For both the SSF and FWS series, outflow concentration of Fe, Mn, Ni and Zn was greater at ~20 mg min^{-1} mass loading than at ~10 mg min^{-1} mass loading (Table 4). For both series, removal efficiency for all metals was less at ~20 mg min^{-1} O & G mass loading than at ~10 mg min^{-1}.

3.2. Effect of oil–water separator on treatment performance

In the SSF series (A) containing the oil–water separator, oxidizing conditions were maintained for all loadings of O & G. The extent of removal for O & G in series A ranged from <1.4–1.9 mg L^{-1} compared to 7.9–11.8 mg L^{-1} in SSF series B without an oil–water separator, with both series operating at an O & G mass loading of ~10 mg min^{-1}. The oil–water separator achieved removal extents ranging from 37.2 to 51.1 mg L^{-1} O & G. Removal rate coefficients for series A ranged from 0.820 to 0.872 d^{-1}, compared to 0.533 to 0.631 d^{-1} for series B. Removal efficiency for series A ranged from 98.1% to 98.6%, compared with 88.1–92.0% for series B operating at ~10 mg min^{-1} O & G loading and 97.2–97.3% for series B operating at ~5 mg min^{-1} loading.

Table 1
Redox potential (mV), dissolved oxygen (D.O.) concentrations (mg L^{-1}), and inflow and outflow concentrations of O & G (mg L^{-1}) at different mass loadings of O & G for series B (SSF) and C (FWS).

	9/27/10[a]	10/11/10[a]	10/25/10[a]	11/8/10[a]	3/14/11[a]	3/21/11[a]	4/4/11[a]	4/11/11[a]
O & G inflow (mg L^{-1})	52.3	49.8	98.7	96.9	101.2	99.3	103.5	98.6
O & G loading (mg min^{-1})								
FWS series	5.45	5.19	10.28	10.10	10.55	10.35	21.57	20.55
SSF series	4.72	4.50	8.91	8.75	9.14	8.97	18.69	17.81
Redox potential (mV)								
FWS series								
Cell 1	115	123	98	69	37	−91	−110	−147
Cell 2	25	−10	20	−30	51	−10	−51	−91
Cell 3	65	59	49	−15	43	19	−67	−49
Cell 4	112	85	72	83	87	75	65	72
SSF series								
Cell 1	159	151	115	73	−5	10	−105	−130
Cell 2	60	78	67	−34	37	−24	−62	−71
Cell 3	49	−15	−47	−23	63	39	22	−32
Cell 4	79	78	118	81	115	87	97	81
D.O. inflow (mg L^{-1})	7.87	7.59	7.99	7.75	7.43	7.88	8.49	8.24
D.O. outflow (mg L^{-1})								
FWS series								
Cell 1	7.11	6.91	6.34	6.12	6.43	5.45	7.13	7.14
Cell 2	7.19	6.72	6.01	6.26	6.79	5.22	7.45	7.46
Cell 3	6.85	6.55	6.15	6.01	6.99	5.61	7.02	7.02
Cell 4	6.69	6.42	6.22	5.81	6.55	5.53	5.62	5.23
SSF series								
Cell 1	6.99	6.78	6.05	5.61	5.98	5.90	7.84	6.52
Cell 2	6.69	6.50	6.23	5.75	6.15	6.12	7.29	6.49
Cell 3	6.58	6.66	6.37	5.50	6.33	5.86	7.32	5.99
Cell 4	6.71	6.71	6.29	6.04	5.84	5.42	5.32	4.52
O & G outflow (mg L^{-1})								
FWS series								
Cell 1	11.5	9.1	21.4	19.8	55.8	60.3	87.6	79.2
Cell 2	7.2	9.8	15.3	12.1	29.4	49.1	75.2	81.1
Cell 3	3.3	5.3	12.0	8.3	14.7	35.2	67.1	70.2
Cell 4	nd	nd	5.5	6.7	8.1	14.6	29.8	35.3
SSF series								
Cell 1	10.4	13.1	30.4	35.1	34.2	43.3	77.2	74.3
Cell 2	4.7	5.9	19.2	21.3	22.9	27.9	67.4	70.9
Cell 3	2.9	4.1	13.3	18.2	19.1	22.1	55.2	68.5
Cell 4	nd	nd	7.9	8.5	9.9	11.8	30.8	31.2

nd = Below detection limit of O & G.
[a] Sampling date. HRT = 2 d for 4/4/11 and 4/11/11; 4 d for all others.

Table 2
Treatment performance for Series A (SSF with oil–water separator), Series B (SSF), and Series C (FWS). Mean (and range).

	Mass loading[a] (mg min^{-1})	O & G inflow conc. (mg L^{-1})	Removal extent (mg L^{-1})	Removal efficiency (%)	Rate coeff. (d^{-1})
FWS series	5.32 (5.19–5.45)	51.1 (49.8–52.3)	1.4 (1.4–1.4)	97.3 (97.2–97.3)	0.899 (0.893–0.905)
	10.32 (10.10–10.55)	99.0 (96.9–101.2)	8.7 (5.5–14.6)	91.2 (85.3–94.4)	0.625 (0.479–0.722)
	21.06 (20.55–21.57)	101.1 (98.6–103.5)	32.6 (29.8–35.3)	67.7 (64.2–71.2)	0.569 (0.514–0.623)
SSF series	4.61 (4.50–4.72)	51.1 (49.8–52.3)	1.4 (1.4–1.4)	97.3 (97.2–97.3)	0.899 (0.893–0.905)
	8.94 (8.75–9.14)	99.0 (96.9–101.2)	9.5 (7.9–11.8)	90.4 (88.1–92.0)	0.588 (0.533–0.631)
	18.25 (17.81–18.69)	101.1 (98.6–103.5)	31.0 (30.8–31.2)	69.3 (68.4–70.2)	0.591 (0.575–0.606)
SSF series w/oil–water separator	8.87 (8.60–9.14)	98.2 (95.2–101.2)	1.5 (1.4–1.9)	98.4 (98.1–98.6)	0.841 (0.820–0.872)

Number of sampling periods = 4 for ~10 mg min^{-1} loading in FWS and SSF series; 2 for all others.
HRT = 2 d for ~20 mg min^{-1} loading in FWS and SSF series; 4 d for all others.
[a] Mass loading was greater for FWS than for SSF series because inflow rate (vol/time) was greater for FWS due to larger water volume in the cell (i.e. to achieve same HRT in both FWS and SSF).

4. Discussion

Oxygen is consumed as oil (i.e. O & G) is aerobically biodegraded (Shin et al., 2000). In the SSF and FWS series (B and C) operating at an O & G mass loading of ~10 mg min^{-1}, dissolved oxygen concentrations in outflow water decreased more in cell 1 (mean decrease from cell inflow to outflow = 0.78 mg L^{-1}) than in cells 2–4 (mean decrease per cell = 0.17 mg L^{-1}, 0.11 mg L^{-1}, 0.03 mg L^{-1}, respectively), which is attributed to a greater amount of O & G removed by biodegradation in cell 1 than in cells 2–4 (Table 1). The lower dissolved oxygen concentration in outflow of cell 4 of each series at O & G loading of ~20 mg min^{-1} compared to ~10 mg min^{-1} is interpreted to be a result of the greater amount of oxygen consumed by biodegradation at the higher mass loading.

Table 3
Inflow and outflow concentrations (mg L^{-1}) of metals for series B (SSF) and C (FWS).

	10/11/10[a]	3/21/11[a]	4/11/11[a]
O & G Loading (mg min^{-1})			
FWS series	5.19	10.35	20.55
SSF series	4.50	8.97	17.81
O & G Inflow Conc. (mg L^{-1})	49.8	99.3	98.6
Fe			
Inflow Conc.	0.311	0.431	0.420
Outflow Conc. FWS series			
Cell 1	0.101	0.199	0.301
Cell 2	0.075	0.081	0.281
Cell 3	0.069	0.101	0.283
Cell 4	0.036	0.053	0.142
Outflow Conc. SSF series			
Cell 1	0.060	0.150	0.328
Cell 2	0.040	0.100	0.274
Cell 3	0.018	0.030	0.291
Cell 4	0.014	0.019	0.170
Mn			
Inflow Conc.	1.247	1.314	1.202
Outflow Conc. FWS series			
Cell 1	0.503	0.700	1.013
Cell 2	0.402	0.549	1.030
Cell 3	0.126	0.421	0.949
Cell 4	0.026	0.150	0.426
Outflow Conc. SSF series			
Cell 1	0.142	0.400	1.062
Cell 2	0.021	0.305	0.991
Cell 3	0.010	0.271	0.527
Cell 4	0.009	0.010	0.202
Ni			
Inflow Conc.	1.212	1.360	1.291
Outflow Conc. FWS series			
Cell 1	1.199	0.809	0.946
Cell 2	0.932	0.477	0.810
Cell 3	0.933	0.244	0.403
Cell 4	0.901	0.220	0.417
Outflow Conc. SSF series			
Cell 1	0.751	0.252	0.809
Cell 2	0.676	0.140	0.572
Cell 3	0.312	0.045	0.180
Cell 4	0.303	0.035	0.163
Zn			
Inflow Conc.	5.71	5.89	5.33
Outflow Conc. FWS series			
Cell 1	4.99	2.11	3.39
Cell 2	3.11	0.598	0.889
Cell 3	3.02	0.126	0.611
Cell 4	2.61	0.103	0.589
Outflow Conc. SSF series			
Cell 1	4.09	1.93	2.69
Cell 2	3.22	0.258	0.837
Cell 3	0.986	0.111	0.453
Cell 4	0.634	0.094	0.423

[a] Sampling date. HRT = 4 d for 10/11/10, 3/21/11; 2 d for 4/11/11.

A change from oxidizing (>-50 mV) to reducing ($\leqslant -50$ mV) conditions in the hydrosoil occurred in both the SSF and FWS series as O & G loading increased from $\sim$10 to 20 mg min^{-1} (Table 1). Wetland cells exposed to the greatest mass loading of O & G (i.e. cell 1 in both series) experienced the greatest decreases in redox potential through the duration of the experiment. This result supports the prediction by Pham et al. (2011) that an increase in mass loading of O & G to the CWTS would result in a change from oxidizing to reducing conditions, with the greatest decrease in redox potential occurring in the upstream cells. In the study by Horner et al. (2011b), reducing conditions were not readily attained in the CWTS; however, O & G mass loading in that study did not exceed $\sim$5 mg min^{-1}. The change from oxidizing to reducing conditions in the hydrosoil with increased mass loading occurring in both the SSF series (cells 1 and 2) and FWS series (cells 1, 2, and 3) resulted in decreased removal efficiency of O & G from the water column. As redox potential decreased from +115 to +10 mV in cell 1 of the SSF series at constant O & G loading of $\sim$10 mg min^{-1}, O & G outflow concentrations increased from 30.4 to 43.3 mg L^{-1} over a period of 5 months. O & G outflow concentrations increased from 21.4 to 60.3 mg L^{-1} as redox decreased from +98 to −91 mV in cell 1 of the FWS series at constant O & G loading of $\sim$10 mg min^{-1} over a 5 month period.

Previous investigations of CWTSs (e.g. Mitsch and Wise, 1998; Mays and Edwards, 2001; Lee and Scholz, 2007) have demonstrated that wetland plant species used in our study are not important sinks for Fe, Mn, Ni, and Zn because they take up only a very small percentage (<1–2%) of these metals. Therefore, we do not consider plant uptake to have played a significant role in the removal of metals in our pilot-scale CWTS. Consistent with design of our pilot-scale CWTS, metals accumulate in hydrosoil and associated plant detritus, where sorption to fallen plant litter can occur (Du Laing et al., 2006; Scholz, 2006; Lee and Scholz, 2007). As plant litter decomposes, the metals can be transformed to more stable and less bioavailable forms (Rodgers and Castle, 2008; Kadlec and Wallace, 2009). Nickel and Zn are transformed by formation of sulfide minerals as sulfate is reduced, which is favored by reducing conditions (Machemer and Wildeman, 1992; Kosolapov et al., 2004). Removal of Ni and Zn was enhanced in both SSF and FWS series of the current investigation as conditions changed from oxidizing to reducing coincident with increased mass loading of O & G. For both the SSF and FWS series, greater removal efficiencies and removal coefficients for Ni and Zn at $\sim$10 mg min^{-1} O & G loading compared to $\sim$5 mg min^{-1} loading (Table 4) are interpreted as the result of lower redox potential promoted by O & G loading. The higher outflow concentrations of Ni and Zn observed at $\sim$20 mg min^{-1} O & G loading compared to $\sim$10 mg min^{-1} loading are attributed to shorter HRT for the $\sim$20 mg min^{-1} loading. As explained in Section 2.1, HRT was controlled by inflow pumping rate, which resulted in greater mass loading of metals with shorter HRT.

The greater removal efficiencies for Fe (FWS series) and Mn (SSF and FWS series) observed with higher redox potentials during $\sim$5 mg min^{-1} O & G loading compared with $\sim$10 mg min^{-1} are consistent with removal of Fe and Mn via oxidative pathways (Benjamin and Leckie, 1981; Rodgers and Castle, 2008). Removal extent of Ni, Zn, and Mn was lower in the SSF series compared to the FWS series at each loading of O & G. At $\sim$5 and $\sim$10 mg min^{-1} O & G loading, Fe removal extent was lower in the SSF series than the FWS series.

Results of this study demonstrate the importance of functional conditions, such as redox potential, in promoting biogeochemical processes for effective treatment in CWTSs and are applicable to the design and construction of full-scale systems. Redox conditions in CWTSs can be adjusted as needed based on characteristics of the water being treated and treatment goals. This pilot-scale study demonstrated that O & G content decreased in the water as it moved through the CWTS, which helped maintain oxidizing conditions in downstream cells. The mass loading of O & G to a CWTS depends on O & G concentration in the inflow water and the rate at which water enters the system, which can be controlled by adjusting the inflow rate. To promote reducing conditions, which are needed to treat constituents such as Ni and Zn through dissimilatory sulfate reduction and production of sulfides, loading of O & G can be increased by decreasing HRT in a full-scale CWTS, as was done in our pilot-scale study. Alternatively, organic carbon amendments such as plant litter can be added to cells to promote reducing conditions. Oxidizing conditions in a CWTS are favorable for biodegradation of O & G and for transfer of metals (e.g., Fe and Mn) that form metal oxides. To promote oxidizing conditions in a CWTS, inflow rate of water containing O & G can be decreased, thus increasing HRT and decreasing O & G mass loading. Alternatively, aeration or rock cascades can be added to a CWTS to promote

Table 4
Metal removal extents, efficiencies, and rate coefficients for Series B (SSF) and Series C (FWS).

Metal	Sampling date	Series	O & G Loading (mg min^{-1})	Inflow conc. (mg L^{-1})	*Extent (mg L^{-1})	Removal (%)	Rate Coeff. (d−1)
Fe	10/11/10	SSF	4.50	0.311	0.014	95.5	0.773
		FWS	5.19	0.311	0.036	88.6	0.544
	3/21/11	SSF	8.97	0.431	0.019	95.7	0.786
		FWS	10.35	0.431	0.053	87.7	0.523
	4/11/11	SSF	17.81	0.420	0.170	59.5	0.452
		FWS	20.55	0.420	0.142	66.2	0.542
Mn	10/11/10	SSF	4.50	1.247	0.009	99.3	1.24
		FWS	5.19	1.247	0.026	97.9	0.970
	3/21/11	SSF	8.97	1.314	0.010	99.2	1.22
		FWS	10.35	1.314	0.150	88.6	0.542
	4/11/11	SSF	17.81	1.202	0.202	83.2	0.891
		FWS	20.55	1.202	0.426	64.5	0.518
Ni	10/11/10	SSF	4.50	1.212	0.303	75.0	0.346
		FWS	5.19	1.212	0.901	25.6	0.074
	3/21/11	SSF	8.97	1.360	0.035	97.4	0.913
		FWS	10.35	1.360	0.220	83.8	0.455
	4/11/11	SSF	17.81	1.291	0.163	87.4	1.04
		FWS	20.55	1.291	0.417	67.7	0.565
Zn	10/11/10	SSF	4.50	5.71	0.634	88.9	0.549
		FWS	5.19	5.71	2.61	54.3	0.196
	3/21/11	SSF	8.97	5.89	0.094	98.4	1.03
		FWS	10.35	5.89	0.103	98.3	1.01
	4/11/11	SSF	17.81	5.33	0.423	92.1	1.27
		FWS	20.55	5.33	0.589	88.5	1.08

* Extent = concentration in series outflow. HRT = 4 d for 10/11/10, 3/21/11; 2 d for 4/11/11.

oxidizing conditions. These design parameters and others, such as hydrosoil composition (i.e. particle size and organic content) and plant selection (i.e. plants that contribute to either oxidizing conditions or reducing conditions in the hydrosoil), can be incorporated in the construction of full-scale CWTSs to promote the biogeochemical processes needed for effective treatment of constituents of concern in a specific water.

Published data on continuous O & G mass loading to a CWTS are sparse. Results from this study support the hypothesis that contaminant removal is dependent on hydraulic loading and inflow concentration of constituents as suggested by Knight et al. (1999). Increased mass loading of O & G resulted in decreased removal of O & G from simulated oilfield produced water, and redox data indicate that O & G mass loading changed environmental conditions in wetland cells. This change in conditions affected removal of not only O & G, but also Ni, Zn, Fe, and Mn. It is not unreasonable to expect a similar change in environmental conditions in a full-scale CWTS when O & G mass loading is concordant with loadings in these pilot-scale experiments. While removal rates are useful for predicting the ultimate surface area and overall footprint of a full-scale CWTS, extents of removal are critical for outflows with risk-based discharge limits. Therefore, it is important to examine removal extents, as well as removal rate coefficients, when using pilot-scale data to design a full-scale CWTS.

5. Conclusions

Concentrations of O & G and metals in simulated oilfield produced water decreased during treatment in both the SSF and FWS series in the pilot-scale CWTS. O & G loading influenced wetland hydrosoil conditions (redox), biogeochemical treatment processes, and treatment performance for O & G and metals in the simulated produced water. As mass loading of O & G increased, development of reducing conditions enhanced removal of Ni and Zn. Removal of O & G, which is favored by oxidizing conditions, declined through the duration of the experiments as reducing conditions developed. With increased O & G mass loading, removal percentage of Mn declined in both series, and Fe removal declined in the FWS series. The SSF series with an oil–water separator demonstrated that removal efficiencies at 10 mg min^{-1} O & G loading can exceed those observed at 5 mg min^{-1} loading without an oil–water separator. At 10 mg min^{-1} O & G loading, lower outflow concentrations were achieved in the SSF series with an oil–water separator compared to the SSF series without an oil–water separator. Results demonstrate that sequential reducing and oxidizing cells in the CWTS were effective in decreasing concentrations of targeted constituents and that treatment performance was strongly influenced as biogeochemical conditions changed in response to O & G mass loading.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.chemosphere.2013.11.027.

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