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# Nitrate removal in surface-flow constructed wetlands treating dilute agricultural runoff in the lower Yakima Basin, Washington

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ABSTRACT

Constructed treatment wetlands (CTWs) have been used effectively to treat a range of wastewaters and non-point sources contaminated with nitrogen (N). But documented long-term case studies of CTWs treating dilute nitrate-dominated agricultural runoff are limited. This study presents an analysis of four years of water quality data for a 1.6-ha surface-flow CTW treating irrigation return flows in Yakima Basin in central Washington. The CTW consisted of a sedimentation basin followed by two surface-flow wetlands in parallel, each with three cells. Inflow typically contained 1–3 mg-N/L nitrate and <0.4 mg-N/L total Kjeldahl N (TKN). Hydraulic loading was fairly constant, ranging from around 125 cm/d in the sedimentation basin to 12 cm/d in the treatment wetlands. Concentration removal efficiencies for nitrate averaged 34% in the sedimentation basin and 90–93% in the treatment wetlands. Total N removal efficiencies averaged 21% and 57–63% in the sedimentation basin and treatment wetlands, respectively. Area-based first-order removal rate constants for nitrate in the wetlands averaged 142–149 m/yr. Areal removal rates for nitrate in treatment wetlands averaged 139–146 mg-N/m$^2$/d. Outflow from the CTW typically contained <0.1 mg-N/L nitrate and <0.6 mg-N/L TKN. Rates of nitrate loss in wetlands were highly seasonal, generally peaking in the summer months (June–August). Nitrate loss rates also correlated significantly with water temperature (positively) and dissolved oxygen (negatively). Based on the modified Arrhenius relationship, $\theta$ for nitrate loss in the wetlands was 1.05–1.09. The CTW also significantly affected temperature and dissolved oxygen concentration in waters flowing through the system. On average, the sedimentation basin caused an increase in temperature (+1.7 °C) and dissolved oxygen (+1.5 mg/L); in contrast the wetlands caused a decrease in temperature (−1.6 °C) and dissolved oxygen (−5.0 mg/L). Results show that CTWs with surface-flow wetlands can be extremely effective at polishing dilute non-point sources, particularly in semi-arid environments where warm temperatures and low oxygen levels in treatment wetland water promote biological denitrification.



## 1. Introduction

Non-point sources account for approximately two-thirds of nutrient loading to the nation's surface waters, and nitrate is a principal pollutant in non-point-source agricultural runoff (Poe et al., 2003; Mitsch et al., 2000). The primary source of nitrate in agricultural runoff is nitrogen (N) fertilizers. About half of applied N-fertilizer is typically taken up by crops, with the remaining N migrating via agricultural runoff into surrounding surface and ground waters, commonly in the form of nitrate (Howarth et al., 1996; Poe et al., 2003). Nitrate poses two key environmental problems: eutrophication of surface waters and contamination of groundwater used for potable supply. Eutrophication is a particular concern in N-limited coastal waters, where the frequency of hypoxic "dead zones" resulting from increased nutrient loading has increased worldwide (Daigle, 2003; Weir, 2005). A critical concern with contaminated groundwater is the toxicity of nitrate to infants (Horne, 2001; USEPA, 2002, 1990).

Constructed treatment wetlands (CTWs) have been shown to be an effective, economical, and ecologically sustainable method to treat N-contaminated wastewaters and non-point sources (Kadlec and Knight, 1996; Horne and Fleming-Singer, 2005). The N biogeochemical cycle within wetland ecosystems is complex and involves numerous transformations including ammonia volatilization, ammonification, N fixation, burial of organic N, ammonia sorption to sediments, nitrification, denitrification, anammox, and

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assimilation (Vymazal, 2007). The primary mechanism for the loss of nitrate in CTWs is denitrification, the microbial reduction of nitrate to dinitrogen gas, which is favored under the anaerobic conditions typically encountered in CTWs (Kadlec and Knight, 1996). Denitrification typically accounts for 60–95% of the nitrate removal in CTWs (Spieles and Mitsch, 2000).

A range of environmental factors influence N transformations in wetland ecosystems, and understanding these factors is important to optimizing nitrate removal in CTWs. Three key factors include N loading, temperature, and dissolved oxygen (DO). Historical observations at a range of CTWs show that levels of a number of pollutants, including nitrate, generally decrease with distance thorough CTWs, suggesting that pollutant removal in CTWs is first order in nature (Kadlec and Knight, 1996). As areal nitrate loading (g-N/m$^2$/d) increases areal removal rates tend to increase. However, as areal removal rates increase, percent removal of nitrate mass and concentration tends to decrease. This relationship has been well documented at a number of experimental wetlands treating nitrate-rich waters (Mitsch and Gosselink, 2000). Since denitrification is a biological process, rates of nitrate loss in CTWs are highly sensitive to temperature. Temperature also affects denitrification by controlling rates of diffusion at the sediment–water interface in wetlands (Crumpton and Phipps, 1992). Denitrification rates in CTWs increase dramatically with temperature, within a lower and upper bounds of around 5 °C and 70 °C, respectively (Vymazal, 2007). Sirivedhin and Gray (2006) documented a two-order of magnitude increase in denitrification rates in wetland sediments when temperature was increased from 4 °C to 25 °C. Being an anoxic process, biological denitrification is also sensitive to DO levels (Firestone, 1982). However, denitrification has been observed in numerous CTWs with measurable levels of DO in wetland water (Kadlec and Knight, 1996; Phipps and Crumpton, 1994). High DO gradients in organic-rich wetland muck and surficial sediments tend to promote both oxic and anoxic biological processes, including denitrification, in close proximity to wetland surface waters.

The objective of this study was to document the effects of N loading, temperature, and DO on nitrate removal in a CTW based on a detailed evaluation of a four-year water quality database (2003–2006). The 1.6 ha vegetated surface-flow CTW, located in the Yakima Basin in central Washington, is unique in that it treats dilute, nitrate-dominated agricultural return flows with nitrate <3 mg-N/L and total Kjeldahl N (TKN) <0.4 mg-N/L. These influent N concentrations are far below those in many CTWs. A review of the North American Treatment Wetland Database (NATWD) by Bachand and Horne (2000a) reported average influent composition to surface-flow CTWs was 48 mg-N/L for TKN, 24 mg-N/L for ammonia, and 9 mg-N/L for nitrate. Results of the study expand the limited number of published case studies of surface-flow CTWs treating low-nitrate agricultural runoff, a non-point source of growing concern and significance.

## 2. Materials and methods

### 2.1. Study site

The Lower Yakima River Basin, located in central Washington, is a vast area stretching over 340 km from the eastside of the Cascade Mountains to the Columbia River. Approximately 1900 km$^2$ of the basin are under agricultural development, much of it irrigated with water distributed by the US Bureau of Reclamation from reservoirs on the upper Yakima River (Romey and Cramer, 2001). In 2001 the Roza and Sunnyside Irrigation Districts, which together serve 71,500 ha in the southeastern Yakima Basin, formed the Roza-Sunnyside Board of Joint Control (RSBOJC). The RSBOJC designed and constructed a pilot treatment wetland, funded as part of the State's total maximum daily load program for the Yakima River, which is listed for sediment, turbidity, and the pesticide DDT (USEPA, 2005).

The RSBOJC CTW has a total treatment area of 16,300 m$^2$ and consists of a sedimentation basin (SB) followed by two surface-flow wetlands in parallel, each with three cells (north wetland: N1, N2 and N3; south wetland: S1, S2 and S3) (Fig. 1 and Table 1). The north and south wetlands have an area of 7950 m$^2$ and 6960 m$^2$, respectively. The wetlands, which were originally planted with 40,000 cattails (*Typha* sp.) and soft stem bulrush (*Scirpus* sp.), currently include a complex mixture of wetland vegetation and open water. The CTW was designed to treat a constant flow of 17 L/s of water pumped from the JD 26.6 lateral of the Granger Drain, which transports runoff from irrigated agricultural and livestock operations to the Yakima River. The total design hydraulic retention time (HRT) in the CTW was approximately eight days and the design hydraulic loading rate ($q$) to the wetlands was approximately 10 cm/d. The CTW is operated during the irrigation season from May to October. Waters in the JD 26.6 lateral contain moderate levels of pollutants typical of irrigation return flows including nitrate (2.0 ± 0.9 mg-N/L; average ± standard deviation, 2003–2006, $n \sim 30$), TKN (0.4 ± 0.1 mg-N/L), total phosphorus (0.13 ± 0.05 mg-P/L), and turbidity (4.9 ± 5.1 NTU). Total N loading is around 30 kg-N/ha/d to the sedimentation basin and 2.5 kg-N/ha/d to the wetlands. Lateral water temperatures typically range from 10 °C to 22 °C and DO levels range from 7 mg/L to 10 mg/L.

### 2.2. Sampling and analysis

This study evaluated four years of water quality and hydraulic data (2003–2006) collected by water quality specialists with the RSBOJC. We omitted 2001–2002, the first two years of CTW operation, since the early water quality data set was somewhat spotty, and since ecosystem development in the initial years of CTW operation typically results in unsustainably elevated nutrient uptake rates as wetland plant biomass is established (Kadlec, 2002). Water quality was monitored at four primary stations: inflow from the JD 26.6 lateral to the sedimentation basin (Inflow), outflow from the sedimentation basin (SB), outflow from the last north wetland cell (N3), and outflow from the last south wetland cell (S3). Monitoring took place approximately every two weeks during the irrigation season from May through October. DO and temperature were measured using a handheld meter (Orion Model, 1230). Nitrate and TKN samples were collected and shipped on ice to a state certified lab (Pacific Northwest Regional Laboratory, US Bureau of Reclamation Water Quality Lab, Boise, Idaho), where they were analyzed using standard method 4500-$NO_3^-$ E for nitrate (cadmium reduction method, detection limit of 0.01 mg-N/L) and standard method 4500-$N_{org}$ B for TKN (macro-Kjeldahl method, detection limit of 0.1 mg-N/L) (APHA, 1998). Flow rate was measured once or twice a month at three stations: outflow from the sedimentation basin with a flow meter attached to the pressurized discharge pipeline to the two wetlands, and outflow from N3 and S3 cells with calibrated flumes installed on each of the surface outflows from the final cells of the north and couth wetlands.

### 2.3. Modeling

Rates of removal for nitrate and total N (calculated as nitrate plus TKN) based on the 2003–2006 data set were quantified using three common approaches for CTWs (Kadlec and Knight, 1996). First, we estimated an area-based first-order removal rate constant for nitrate ($K_N$) and total N ($K_{TN}$) using the $K$–$C^*$ model assuming

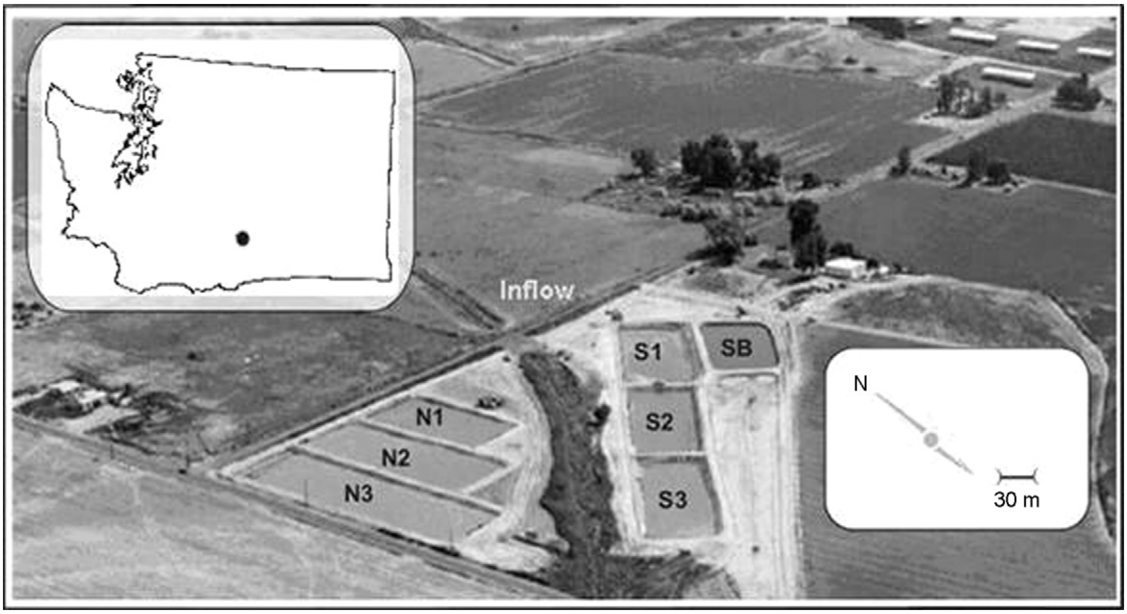


**Fig. 1.** Aerial view of the RSBOJC CTWs (prior to planting). The JD 26.6 lateral flows from north to south between the north wetland cells (N1, N2 and N3) and south wetland cells (S1, S2 and S3). Water is diverted from the drain (Inflow) and pumped at a constant rate to a sedimentation basin (SB). The flow is then divided and pumped into the first cell of each treatment wetland (N1 and S1). The flow exits the last cell of each treatment wetland (N3 and S3) back to the lateral by gravity. Sampling sites include SB inflow, SB outflow (same as wetland inflow to N1 and S1), N3 outflow and S3 outflow.

plug flow conditions:

$$K = -q \times \ln\left(\frac{C_{\mathrm{out}} - C*}{C_{\mathrm{in}} - C*}\right) \tag{1}$$

where $K$ is the first-order removal rate constant (m/yr), $q$ is the hydraulic loading rate (m/yr), $C_{\mathrm{in}}$ and $C_{\mathrm{out}}$ are the inlet and outlet concentrations of nitrate or total N (mg-N/L), and $C^*$ is the background concentration (mg-N/L). The $C^*$ for nitrate was zero, and the $C^*$ for total N, based on outflow data from the RSBJC CTW, was 0.3 mg-N/L. $K_{\mathrm{N}}$ values were normalized to 20 °C ($K_{\mathrm{N\text{-}20}}$) based on Eq. (4) assuming a $\theta$ value of 1.09 for denitrification in wetlands (Kadlec and Knight, 1996). Second, we estimated the concentration removal efficiency (%):

$$\text{removal efficiency} = \frac{C_{\mathrm{in}} - C_{\mathrm{out}}}{C_{\mathrm{in}}} \times 100 \tag{2}$$

Finally, we estimated the areal removal rate (mg-N/m$^2$/d):

$$\text{removal rate} = q \times (C_{\mathrm{in}} - C_{\mathrm{out}}) \tag{3}$$

The effect of temperature on the first-order removal rate constant for nitrate was modeled based on the modified Arrhenius relationship:

$$K(t) = K(20)\theta^{(t-20)} \tag{4}$$

where $K(t)$ and $K(20)$ are the first-order removal rate constants (m/yr), $t$ is temperature (°C), and $\theta$ is an empirical temperature coefficient (Kadlec and Knight, 1996). A linearized form of Eq. (4) was used to estimate parameters of the model from our data set:

$$\log[K(t)] = \log\theta(t-20) + \log[K(20)] \tag{5}$$

Values of $\log[K(t)]$ versus $(t-20)$ were plotted and fit with a linear regression. The resulting slope and intercept were equal to $\log\theta$ and $\log[K(20)]$, respectively.

### 2.4. Data and statistical analysis

The water quality data set consisted of temperature, DO, nitrate, and TKN for 2003–2006 at four stations (Inflow, SB, N3 and S3; $n$ = 30–35). Flowrate data were collected less frequently at three

**Table 1**
Site design characteristics for the RSBOJC constructed treatment wetlands.

| Cell | Length (m) | Width (m) | Average depth (m) | Area (m$^2$) | Flow rate (L/s) | $q$ (cm/d) | HRT (d) |
|---|---|---|---|---|---|---|---|
| *Sedimentation basin* | | | | | | | |
| SB | 61.0 | 23.0 | 1.7 | 1400 | 17 | 105 | 1.6 |
| *North wetland* | | | | | | | |
| N1 | 61.0 | 30.5 | 0.30 | 1860 | | | |
| N2 | 83.8 | 30.5 | 0.68 | 2560 | | | |
| N3 | 115.8 | 30.5 | 0.74 | 3530 | | | |
| Total | | | | 7950 | 8.5 | 9.2 | 6.7 |
| *South wetland* | | | | | | | |
| S1 | 76.2 | 30.5 | 0.75 | 2320 | | | |
| S2 | 76.2 | 30.5 | 0.56 | 2320 | | | |
| S3 | 76.2 | 30.5 | 0.69 | 2320 | | | |
| Total | | | | 6960 | 8.5 | 10.6 | 6.3 |

**Table 2**
Summary of flow rate, temperature and DO data for the RSBOJC constructed treatment wetlands.

| Inflow rate (L/s) | Outflow rate (L/s) | Average $q$ (cm/d) | Temperature (°C) | | | DO (mg/L) | | |
|---|---|---|---|---|---|---|---|---|
| | | | In | Out | ΔTemp | In | Out | ΔDO |
| *Sedimentation basin* | | | | | | | | |
| 20.0[a] | 20.0 (7.8) | 123.5 | 16.1 (2.5) | 17.7 (3.4) | 1.7 (1.8) | 9.3 (3.2) | 10.8 (3.5) | 1.5 (3.5) |
| *North wetland* | | | | | | | | |
| 10.0[a] | 6.8 (3.7) | 10.9 | 17.1 (3.0) | 15.3 (3.9) | −1.8 (2.2) | 11.1 (3.7) | 6.3 (2.5) | −5.0 (4.0) |
| *South wetland* | | | | | | | | |
| 10.0[a] | 9.1 (5.5) | 12.4 | 17.4 (3.1) | 15.9 (4.0) | −1.6 (2.4) | 11.3 (3.7) | 6.4 (2.2) | −4.9 (4.0) |

Values are averages and standard deviations (in parentheses) for 2003–2006 data set; $n$ = 22–29 for flow rate; $n$ = 30–35 for temperature and DO.
Sedimentation basin average $q$ based on average outflow rate; wetland average $q$ values based on wetland inflow rates.
[a] Assumed values. Outflow from sedimentation basin is evenly split between the north and south wetlands.

stations (SB, N3 and S3; $n$ = 22–29). While inflow to each of the two treatment wetlands was not directly measured (i.e., at N1 and S1), the pipeline system was designed to evenly split sedimentation basin outflow between the two wetlands. We estimated an average $q$ for the entire data set, and then applied that average $q$ to the nitrate and total N concentration data sets to estimate the removal rates based on Eqs. (1) and (3) for the three treatment components of the CTW (sedimentation basin, north wetland and south wetland). The average $q$ to the sedimentation basin was estimated as the average outflow (Table 2) divided by the design area of the basin. The average $q$ to the wetlands was based on half the sedimentation basin inflow divided by the design area. To evaluate if the impacts of the sedimentation basin, the north wetland, and the south wetland on water quality (temperature, DO, nitrate and total N) were statistically significant ($p < 0.05$), a two-tailed $t$-test (paired two sample for means) was performed on inlet and outlet concentrations for each of the three treatment components. In addition, a two-tailed $t$-test (two-sample assuming unequal variances) was performed on outlet concentrations (temperature, DO, nitrate and total N) of the two treatment wetlands to determine if the wetlands acted in a statistically similar fashion. To elucidate controlling factors on nitrate removal in the CTW, a correlation matrix ($r$ value of linear regression) was developed between $K_N$, inflow nitrate concentration, inflow temperature, outflow temperature, inflow DO, and outflow DO for the three treatment components.

## 3. Results

### 3.1. Hydrology, temperature and DO

Inflow to the CTW for the four-year data set averaged 20.0 L/s (Table 2), slightly higher than the design inflow rate of 17 L/s (Table 1). Inflow to each wetland, which was not measured directly, was estimated at 10.0 L/s, yielding an average $q$ of 10.9 cm/d in the north wetland and 12.4 cm/d in the south wetland. The sedimentation basin resulted in a statistically significant increase in average temperature (+1.7 °C) and DO (+1.5 mg/L) (Table 2). In contrast, both wetlands resulted in a significant drop in average temperature (−1.7 °C) and DO (−5 mg/L). Temperature and DO were not significantly different in outflow from the north and south wetlands. Seasonal trends were apparent in wetland temperature and DO (Fig. 2A and B). Inflow and outflow temperatures increased from 12–14 °C in the spring, peaked to 20–23 °C in early July, then dropped back down to <15 °C in the fall. Differences between inflow and outflow temperatures were most pronounced in the later part of the irrigation season (August–October). DO levels in wetland inflow (same as sedimentation outflow) were somewhat variable ranging from the extremes of 3 mg/L to 18 mg/L and averaging around 11 mg/L. DO levels in wetland outflow tended to mirror, in an opposite fashion, those of temperature, particularly in 2005 and 2006. In those years outflow DO dropped from around 10 mg/L in the spring, to a minimum of ∼4–5 mg/L in the summer, to around 8 mg/L in the fall. Differences between inflow and outflow DO were most pronounced in the summer months.

### 3.2. Nitrate and total nitrogen concentrations

Average annual total N levels entering the CTW over the study period (2003–2006) varied from 1.8 mg-N/L to 2.7 mg-N/L, and were dominated by nitrate (76–86%) (Fig. 3). Average annual total N levels in sedimentation basin outflow and wetland outflow ranged from 1.3 mg-N/L to 2.5 mg-N/L and 0.6 mg-N/L to 1.0 mg-N/L, respectively. Average annual nitrate levels in wetland outflow were consistently <0.4 mg-N/L. Waters were progressively enriched with organic N relative to nitrate as they flowed through the CTW; the average annual percent of TKN as total N increased from 14–24% in inflow, to 20–44% in sedimentation basin outflow, to 61–94% in wetland outflow. This phenomenon was a combined effect of increasing TKN concentrations and decreasing nitrate concentrations through the CTW (Fig. 3). Total N and nitrate in wetland inflow tended to decrease as the irrigation season progressed (Fig. 2C and D). Nitrate levels in 2004, for example, dropped from around 2 mg-N/L in the spring to around 0.5 mg-N/L in the late summer and fall. Nitrate levels in wetland effluent were commonly below detection limit (0.01 mg-N/L). Statistical analysis confirmed that decreases in nitrate and total N through the sedimentation basin and both wetlands were significant, and that there was no statistical difference between nitrate and total N levels in outflow from the north and south wetlands.

### 3.3. Nitrate and total nitrogen removal rates

Area-based first-order removal rates for nitrate averaged 187 m/yr for the sedimentation basin, 142 m/yr in the north wetland, and 149 m/yr in the south wetland (Table 3). Average removal rates increased somewhat when they were normalized to 20 °C ($K_{N\text{-}20}$). Average concentration removal efficiencies were relatively low in the sedimentation basin (34%) but high in the wetlands (90–93%); however, on an areal basis removal rates were higher in sedimentation basin (837 mg-N/m$^2$/d) compared to the wetlands (139–146 mg-N/m$^2$/d). On average the CTW removed 94% of nitrate on a concentration basis. Removal rates dropped when put in terms of total $N$, but removal trends in the sedimentation basin versus the wetlands were similar (Table 4). For example, average total $N$ concentration removal efficiencies were 21% in the sedimentation basin, 57–63% in the wetlands, and 68% for the entire CTW. $K_N$ values showed a strong seasonal trend (Fig. 4). Rates were generally lower in April and early May (<100 m/yr), peaked in July (200–250 m/yr), and then remained high or decreased somewhat

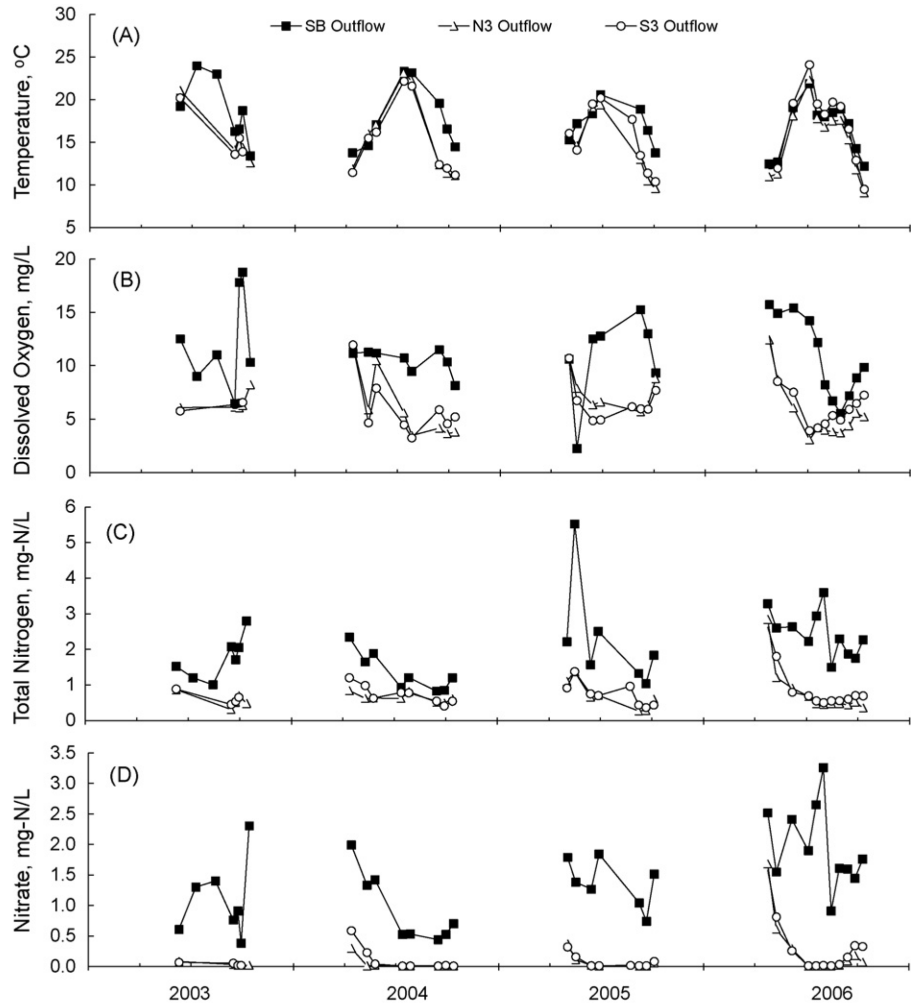


**Fig. 2.** Water quality (temperature, DO, total N and nitrate) in influent and effluent of the RSBOJC treatment wetlands. SB outflow is from sedimentation basin to wetland cells N1 and S1; N3 outflow is from last cell of north treatment wetlands back to JD 26.6 lateral; S3 outflow is from last cell of south treatment wetlands back to JD 26.6 lateral.

in September and October. Temperature dependency of $K_N$ in the north and south wetlands was modeled based on a linearized form of modified Arrhenius relationship (Fig. 5). The model had a fairly low $r^2$ (0.25) but was statistically significant ($p < 0.01$). Based on the model, the $\theta$ value was 1.09 and the $K_{N\text{-}20}$ was 175 m/yr, which was similar in magnitude to the average $K_{N\text{-}20}$ estimated from the data set (196 m/yr and 192 m/yr; Table 3).

Values of $K_N$ were found to correlate significantly with a number of parameters (Table 5). In the sedimentation basin, $K_N$ correlated positively with outflow temperature. A number of parameters covaried significantly including inflow and outflow temperature and inflow and outflow DO. Inflow DO also negatively correlated with outflow temperature. In the wetlands, $K_N$ correlated with inflow temperature (positive) and outflow DO (negative) (Table 5

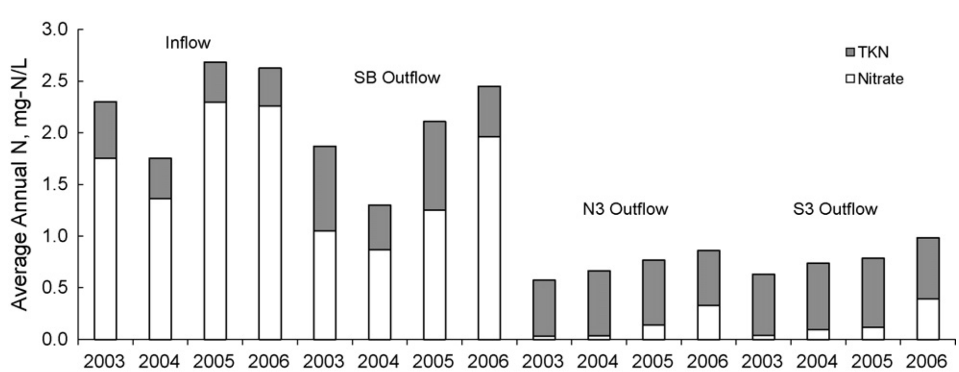


**Fig. 3.** Average annual concentrations of nitrate and TKN over the wetland operating months (May–October): Inflow (inflow to sedimentation basin from JD 26.6 drain); SB outflow (outflow from sedimentation basin to wetland cells N1 and S1); N3 outflow (outflow from last cell of north treatment wetlands back to JD 26.6 drain); S3 outflow (outflow from last cell of south treatment wetlands back to JD 26.6 drain).

**Table 3**
Summary of nitrate removal in the RSBOJC constructed treatment wetlands.

| Nitrate | | | | | |
|---|---|---|---|---|---|
| Concentration (mg-N/L) | | $K_N$ (m/yr) | $K_{N\text{-}20}$ (m/yr) | Removal efficiency (%) | Removal rate (mg-N/m²/d) |
| In | Out | | | | |
| *Sedimentation basin* | | | | | |
| 2.0 (0.86) | 1.4 (0.74) | 187 (163) | 237 (183) | 34 (27) | 837 (884) |
| *North wetland* | | | | | |
| 1.4 (0.73) | 0.1 (0.32) | 142 (54) | 196 (80) | 93 (14) | 139 (75) |
| *South wetland* | | | | | |
| 1.3 (0.74) | 0.2 (0.32) | 149 (68) | 192 (84) | 90 (15) | 146 (83) |

Values are averages and standard deviations (in parentheses) for 2003–2006 data set; $n = 30–35$.
$K$ values estimated using average $q$ values from Table 2.
$K_{N\text{-}20}$ based in a $\theta$ value of 1.09.

**Table 4**
Summary of total nitrogen removal in the RSBOJC constructed treatment wetlands.

| Total nitrogen | | | | |
|---|---|---|---|---|
| Concentration (mg-N/L) | | $K_{TN}$ (m/yr) | Removal efficiency (%) | Removal rate (mg-N/m²/d) |
| In | Out | | | |
| *Sedimentation basin* | | | | |
| 2.4 (0.92) | 2.0 (0.96) | 112 (130) | 21 (26) | 631 (1008) |
| *North wetland* | | | | |
| 2.1 (0.95) | 0.7 (0.47) | 73 (44) | 63 (18) | 148 (92) |
| *South wetland* | | | | |
| 2.0 (0.96) | 0.8 (0.45) | 63 (33) | 57 (22) | 151 (106) |

Values are averages and standard deviations (in parentheses) for 2003–2006 data set; $n = 30–35$.
$K$ values estimated using average $q$ values from Table 2.

and Fig. 6). Inflow temperature was found to correlate with outflow temperature (positive) and outflow DO (negative). Outflow temperature also appeared to correlate negatively with outflow DO. Unlike the sedimentation basin, inflow and outflow DO did not covary in the wetlands. Values of $K_N$ did not correlate with inflow nitrate concentration, an analog for nitrate loading presuming low variation in $q$ over time, in the sedimentation basin or the wetlands.

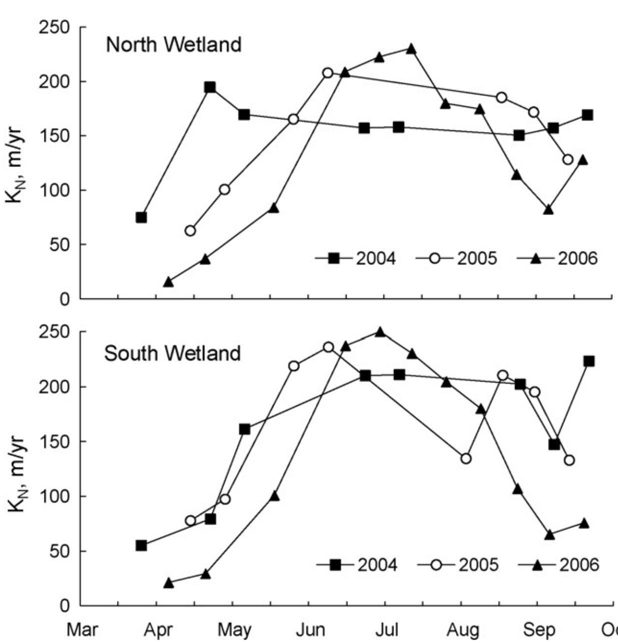


**Fig. 4.** Seasonal pattern of $K_N$ in north and south treatment wetlands for 2004, 2005 and 2006.

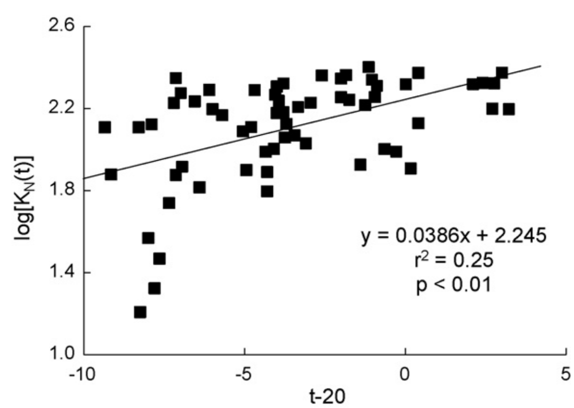


**Fig. 5.** $K_N$ dependence on temperature based on the modified Arrhenius equation. Line is linear regression of data for both north and south constructed treatment wetlands for 2003–2006 data set. Units of $K_N$ are m/yr. Slope equals $\log\theta$ ($\theta = 1.09$) and $x$-intercept equals $\log[K_N(20)]$ ($K_N(20) = 175$ m/yr).

## 4. Discussion

### 4.1. Hydrology, temperature and DO

Average hydraulic loading to the wetlands, 10.9 cm/d in the north wetland and 12.4 cm/d in the south wetland, was relatively high. Typical values for surface-flow wetlands treating nitrate-dominant wastewaters are 1–10 cm/d (Kadlec and Knight, 1996). Mitsch and Gosselink (2000) reported a hydraulic loading rate of 5.4 ± 1.7 cm/d (average ± standard error) for over a dozen North American CTWs. Based on a comparison of inflow and outflow rates, average net water loss, which included evapotranspiration, bank losses, infiltration and precipitation, was 3.5 cm/d in the north wet-

**Table 5**
Correlation matrix between $K_N$ and key water quality parameters for the RSBOJC constructed treatment wetlands.

| | $K_N$ | Inflow nitrate | Inflow temp | Outflow temp | Inflow DO |
|---|---|---|---|---|---|
| *Sedimentation basin* | | | | | |
| Inflow nitrate | −0.14 | 1.00 | | | |
| Inflow temp | 0.32$^{\dagger}$ | −0.06 | 1.00 | | |
| Outflow temp | 0.37$^{*}$ | −0.26 | 0.86$^{**}$ | 1.00 | |
| Inflow DO | −0.16 | 0.21 | −0.06 | −0.40$^{*}$ | 1.00 |
| Outflow DO | 0.10 | −0.09 | 0.21 | 0.09 | 0.43$^{*}$ |
| *North wetland* | | | | | |
| Inflow nitrate | 0.02 | 1.00 | | | |
| Inflow temp | 0.44$^{*}$ | −0.29 | 1.00 | | |
| Outflow temp | 0.33 | −0.03 | 0.83$^{**}$ | 1.00 | |
| Inflow DO | −0.13 | −0.01 | 0.04 | 0.03 | 1.00 |
| Outflow DO | −0.61$^{**}$ | 0.28 | −0.53$^{**}$ | −0.32$^{\dagger}$ | 0.20 |
| *South wetland* | | | | | |
| Inflow nitrate | −0.15 | 1.00 | | | |
| Inflow temp | 0.66$^{**}$ | −0.30 | 1.00 | | |
| Outflow temp | 0.55$^{**}$ | 0.14 | 0.79$^{***}$ | 1.00 | |
| Inflow DO | −0.03 | −0.03 | 0.08 | 0.01 | 1.00 |
| Outflow DO | −0.75$^{**}$ | 0.30$^{\dagger}$ | −0.61$^{**}$ | −0.52$^{**}$ | 0.20 |

Positive values indicate positive correlation; negative values indicate negative correlation. $n \sim 30$.
$^{\dagger}$ $p < 0.10$.
$^{*}$ $p < 0.05$.
$^{**}$ $p < 0.01$.

land and 1.1 cm/d in the south wetland. These losses are higher than the average April–October net evaporative loss of 0.4 cm/d (80% of pan evaporation minus precipitation) calculated from historical meteorological data for the region. Thus both wetlands, particularly the north wetland, appeared to be losing water through bank loss and/or infiltration.

In northern climates, the dominant processes controlling water temperature in wetlands are energy uptake from incidental solar radiation, convective heat transfer from the atmosphere, and energy loss to the atmosphere through evaporation (Kadlec and Knight, 1996). Because wetland plants shade water from incoming solar radiation and dissipate energy through transpiration, evaporative cooling dominates the water energy balance in wetlands. As a result, average daily outflow temperatures are generally lower than inflow temperatures, particularly in arid climates (Kadlec, 2006). Such was the case in the RSBOJC wetlands which on average showed a nearly 2 °C drop in temperature between inflow and outflow (Table 2). Temperature differential was as high as 4–7 °C in the fall of 2004 and 2005 (Fig. 2A). The opposite dynamics were at work in the non-vegetated sedimentation basin with an uptake of solar radiation leading to an average increase in temperature between inflow and outflow of almost 2 °C.

Greater solar radiation input to the sedimentation basin also facilitated algal productivity and associated DO production during photosynthesis, resulting in the observed increase through the sedimentation basin to DO levels as high as 18 mg/L (Fig. 2B). In the wetlands, microbial decay of organic matter in shaded and shallow waters led to elevated oxygen consumption and a decrease in DO concentration in wetland waters by an average 5 mg/L (Table 2). A number of researchers have observed drops in DO in surface-flow CTWs similar to those in this study. Bachand and Horne (2000b) found that mean DO dropped from 9.6 mg/L to 5.2 mg/L through replicate experimental macrocosm wetlands treating high-nitrate river water. Thullen et al. (2002) measured mean DO levels of 1–2 mg/L in outflow from vegetated cells and 4–6 mg/L in outflow from hummock hemi-marsh cells (wetland plants grown on raised beds with around 80% open water) in experimental wetlands treating ammonia dominated secondary effluent; influent DO was not reported but was presumably near saturation (8–10 mg/L). Correlation analyses also illustrated the contrasting influence that the sedimentation basin and wetlands had on water passing through the systems, particularly with respect to DO (Table 5). In the sedimentation basin, outflow DO correlated significantly with inflow DO but not with inflow or outflow temperature. In the wetlands, with their longer residence time and high biological activity, the opposite was observed with outflow DO correlating with temperature in inflow and/or outflow.

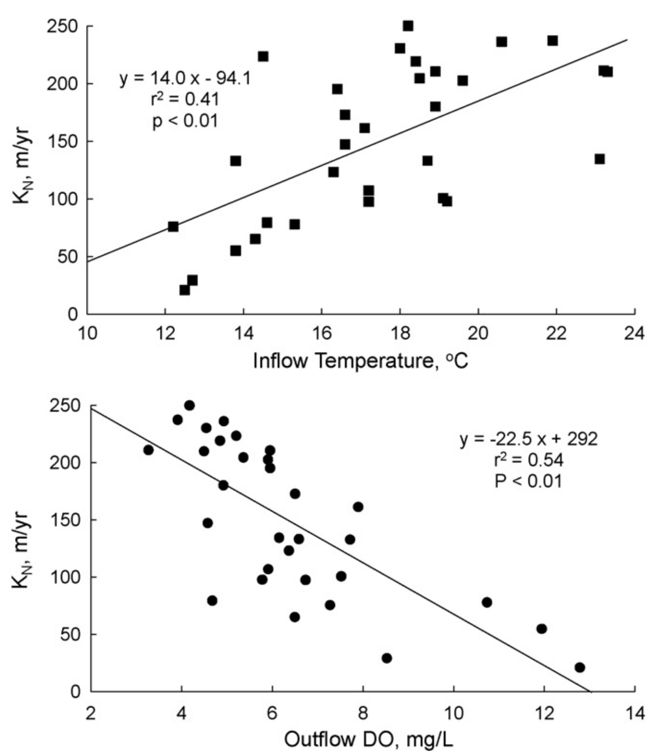


**Fig. 6.** $K_N$ as a function of inflow temperature (top) and outflow DO (bottom) for the south constructed treatment wetland for 2003–2006 data set. Lines are linear regression of data.

### 4.2. Nitrogen removal rates

Area-based first-order removal rates estimated for the treatment wetlands were high compared to values reported in the literature. Average values for $K_N$ and $K_{TN}$ were around 145 m/yr and 68 m/yr, respectively (Table 3). Typical values for surface-flow CTWs with similar nitrate concentration in inflow reported by Kadlec and Knight (1996) range from 10 m/yr to 60 m/yr for $K_N$ and 5 m/yr to 20 m/yr for $K_{TN}$. Removal efficiencies of >90% for nitrate and ~60% for total nitrogen, and areal removal rates of 100–200 mg-N/m$^2$/d for nitrate, were comparable to those reported for other surface-flow CTWs treating nitrate-dominated wastewaters in semi-arid climates. Pilot-scale testing in the Prado Wetlands in Southern California measured around 80% nitrate removal efficiencies during summer operations; average areal removal rates for nitrate were around 500 mg-N/m$^2$/d (Horne, 2001; Reilly et al., 2000). In the San Joaquin Marsh, a pond/marsh CTW in Southern California, removal efficiencies averaged 80% for nitrate and 60% for total N, and areal removal rates were around 300 mg-N/m$^2$/d (Fleming-Singer and Horne, 2006; Horne, 2001). This areal removal rate was similar to average rates measured at the RSBOJC CTW, particularly when they were estimated for the composite sediment basin/wetland system (240–260 mg-N/m$^2$/d). As observed at the RSBOJC CTW, outflow from the San Joaquin Marsh was also enriched with organic N, supporting the generally accepted fact that wetlands are sinks for inorganic nutrients (e.g., nitrate) but sources of organic material (e.g., organic N) (Mitsch and Gosselink, 2000). Nitrate removal rates observed in the RSBOJC wetlands were higher than those predicted by an empirical nitrate retention model developed for river-fed CTWs in the Midwestern US (Mitsch and Gosselink, 2000). The RSBOJC wetlands were loaded with around 40 g-N/m$^2$/yr of nitrate. At this loading rate the model predicted a concentration removal efficiency of 55% and an areal removal rate of 16 g-N/m$^2$/yr. Actual removal rates were >90% and around 25 g-N/m$^2$/yr. The underestimate was likely a result of the warmer temperatures and non-winter operation at the RSBOJC wetlands.

### 4.3. Influence of nitrate concentration, temperature and oxygen on nitrogen removal

Numerous studies have shown that denitrification rates in CTWs increase with increasing nitrate concentration in inflow, and nitrate removal in wetlands is typically modeled as a first-order process relative to inflowing nitrate concentration (Kadlec and Knight, 1996). Some studies have not found this relationship, arguing that kinetic predictions show that biological denitrification is not limited at the nitrate levels typical of CTWs (Bachand and Horne, 2000b). In our study, values of $K_N$ in wetlands did not correlate with inflow nitrate concentration. However, the range in inflow concentrations was small, typically from around 1 mg-N/L to 3 mg-N/L, and this may have masked a potential relationship between inflowing nitrate concentration and nitrate removal rates.

While $K_N$ in wetlands showed no correlation with inflow nitrate concentration, there was a significant correlation with inflow and/or outflow temperature (Table 5). This was to be expected, since biological denitrification is strongly affected by temperature. Results from our modeling of temperature effects on area-based first-order removal yielded a higher $K_{N\text{-}20}$ (175 m/yr) than the 'central tendency' value for surface-flow CTWs (35 m/yr) reported by Kadlec and Knight (1996). But our $\theta$ value for nitrate removal (1.09) was similar to values for denitrification in treatment wetlands reported by Kadlec and Knight (1996) (1.09) and Bachand and Horne (2000b) (1.15–1.18). Our temperature model appeared to overestimate $K_N$ for a handful of data from a particularly cool early spring in 2004 (four data points in the lower left-hand section of Fig. 5). However, the model did predict removal rates well during cold fall weather. Clearly some other environmental factor(s) was limiting nitrate removal during spring 2004. DO was extremely elevated in both wetland inflow and outflow during this period with some of the highest values recorded for the entire 2003–2006 data set (12–16 mg/L in late April, 2004; 8–15 mg/L in early May, 2004). These high DO conditions may have constrained nitrate removal by robbing the wetlands of the anoxic conditions that favor biological denitrification. Carbon limitation has also been shown to limit denitrification in CTWs (Bachand and Horne, 2000b; Reilly et al., 2000), and this too may have played a role in limiting nitrate removal rates early in the growing season. Excluding the spring 2004 data points yielded a $\theta$ of 1.05, a value somewhat closer to those sited by Crumpton and Phipps (1992) (1.07) and Fleming-Singer and Horne (2006) (1.04–1.07).

As noted by Spieles and Mitsch (2000), few studies have evaluated how DO in wetland water regulates denitrification since nitrate loss in wetlands has been observed in CTWs under well oxygenated conditions. A more important driver of denitrification is the presence of an anoxic muck layer rich in bioavailable carbon (Sirivedhin and Gray, 2006; Fleming-Singer and Horne, 2006). Our data set allowed for a comparison of DO and nitrate removal in wetlands, and of the environmental factors we evaluated, $K_N$ most strongly correlated (negatively) with DO in outflow (Table 5). This contrasts with observations by Bachand and Horne (2000a,b) who found that rates of denitrification did not correlate with DO in pilot-scale surface-flow wetlands treating nitrate-dominated waters. This discrepancy may be related to the high hydraulic loading rates used in their study (28–167 cm/d). How important bulk DO concentration in wetland water is as a driver of denitrification in the wetlands is uncertain. In the RSBOJC wetlands, DO in outflow also significantly covaried (negative) with inflow and outflow temperature, which is a strong controller of denitrification rates. We hypothesize that high water temperatures enhanced rates of microbial oxygen uptake while lowering DO solubility, and the combination of high temperatures and low DO together result in enhanced rates of nitrate removal in the wetlands during warm summer months (Fig. 4).

## 5. Conclusion

Based on a detailed evaluation of a four-year water quality data set, we formulated the following four key conclusions:

(1) Even at relatively low influent nitrate levels (<3 mg-N/L), CTWs can be extremely effective in removing N pollution, though areal removal rates may be comparatively low. Concentration removal efficiencies in treatment wetlands consistently exceeded 90% for nitrate and 60% for total N. Average areal removal rates for nitrate and total N were 100–200 mg-N/m$^2$/d. While nitrate areal removal rates were comparable to typical CTWs, total N areal removal rates were far lower. For example, areal removal rates for CTWs in the North American Treatment Wetland Database averaged 125 mg-N/m$^2$/d ($n$ = 51) for nitrate and 513 mg-N/m$^2$/d ($n$ = 37) for total N (Bachand and Horne, 2000a).

(2) Sedimentation basins, while primarily designed to capture suspended solids and prevent excessive sediment build-up in treatment wetland, yielded removal of nitrate and total N in the range of 20–30% on a concentration basis. With their small surface area, this translated to relatively high N removal rates on an areal basis (600–800 mg-N/m$^2$/d). However, like wetlands,

at times the sedimentation basin acted as a source of organic N.

(3) Nitrate removal rates were highly sensitive to temperature and exhibited seasonal trends. Removal rates in warm summer months (June–August) were 2–4 times higher than in cooler months. Lowest rates were observed in the spring. Temperature effects on the area-based first-order removal rate constant for nitrate in treatment wetlands, estimated using the modified Arrhenius equations, resulted in a $\theta$ value of 1.05–1.09.

(4) CTW unit processes affected water temperature and DO in differing ways. Sedimentation basins tended to increase temperature and DO, while vegetated wetlands tended to decrease temperature and DO. In addition, temperature and DO levels in outflow correlated more closely to inflow conditions in sedimentation basins compared to treatment wetlands.

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