Available online at www.sciencedirect.com
SCIENCE DIRECT®
Ecological Engineering 26 (2006) 100–112
ECOLOGICAL ENGINEERING
www.elsevier.com/locate/ecoleng

Plant species and temperature effects on the k–C^* first-order model for COD removal in batch-loaded SSF wetlands

Otto R. Stein [a,*], Joel A. Biederman [b], Paul B. Hook [c], Winthrop C. Allen [d]

[a] *Department of Civil Engineering and the Center for Biofilm Engineering, Montana State University, Bozeman, MT 59717, USA*
[b] *Department of Mathematics, Suffield Academy, Suffield, CT 06078, USA*
[c] *Center for Biofilm Engineering and Affiliate Faculty Department of Land Resources and Environmental Science, Montana State University, Bozeman, MT 59717, USA*
[d] *The GEL Group, 2040 Savage Road, Charleston, SC 29417, USA*

Received 26 May 2005; accepted 3 July 2005

Abstract

The modified k–C^* first-order degradation model proposed by Kadlec and Knight [Kadlec, R.H., Knight, R.L., 1996. Treatment Wetlands. Lewis Publishers, Boca Raton, FL] was fit to 192 data sets of COD concentration versus time measured in batch-loaded wetland microcosms. The time series sets were divided into four replicates of four plant species treatments; *Carex utriculata* (sedge), *Schoenoplectus acutus* (bulrush), *Typha latifolia* (cattail) and unplanted controls housed in a controlled-environment greenhouse in which temperature was cycled in 4 °C increments from 24 to 4 °C and back to 24 °C over a yearlong period. One 20-day batch incubation was conducted at each temperature setting during which seven chemical oxygen demand (COD) samples were drawn from each of 16 wetland columns. Non-linear mixed effects regression was used to fit parameters of the model.

Best-fit values of the rate parameter k and the background concentration C^* varied significantly by plant species and greenhouse temperature setting. An Arrhenius relationship was used to assess the effect of temperature on these parameters. Species greatly influenced the value of volumetric rate parameter at 20 °C (k_{20}) and ranked *Carex* > *Schoenoplectus* > *Typha* > unplanted control (0.925, 0.743, 0.612 and 0.366 day^{-1}, respectively). All displayed decreasing values for increasing temperature but species variation was much less ($\theta_k = 0.945$, 0.957, 0.953 and 0.936, respectively). Background COD concentration values at 20 °C (C^*_{20}) ranked *Carex* < *Schoenoplectus* < *Typha* < unplanted control (42, 46, 66, 67 $mg\,L^{-1}$, respectively) but seasonal variation was mixed ($\theta_{C^*} = 1.029$, 0.999, 0.958 and 0.935, respectively). The results indicate that (1) seasonal variation of performance is plant-species specific; (2) singly, the rate constant k cannot capture the variation in performance due to temperature as much of the variation is reflected in the C^* and (3) there are strong interactions between values of k and C^*.

Keywords: Wastewater; Treatment; Constructed wetland; *Carex*; *Schoenoplectus*; *Typha*

* Corresponding author. Tel.: +1 406 994 6121; fax: +1 406 994 6105.
E-mail address: ottos@ce.montana.edu (O.R. Stein).

0925-8574/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.ecoleng.2005.07.001

1. Introduction

Efforts to predict removal of organic matter (OM) by constructed wetlands (CWs) rely largely on simplified mathematical models calibrated against performance data. While general guidelines and maximum loading rate criteria are still popular and reasonably effective for CW design (IWA, 2000; USEPA, 2000), there is a general recognition that models that are at least superficially related to microbial process kinetics offer a better design framework. The first-order decay model is the simplest of these (USEPA, 1988). This model lumps all biological and physical influences on organic matter removal and recycling into one rate parameter (k) and predicts that influent organic matter concentration will asymptotically approach zero.

Recognizing the shortcomings of a one-parameter model and to better fit available data, Kadlec and Knight (1996) proposed a modified first-order model, often called the k–C^* model. This model allows for a background or residual concentration (C^*), a non-zero lower limit that is approached asymptotically in lieu of the first-order model approach to zero. Conceptually, the inclusion of C^* accounts for the generation of OM within the wetland, input from atmospheric or ground sources, and existence of a recalcitrant fraction of influent OM. In the absence of data quantifying these OM components, C^* may be considered an empirical data-fitting parameter (Kadlec, 2000).

Other model types, especially those employing Monod kinetics (Mitchell and McNevin, 2001; Wynn and Liehr, 2001; Rousseau et al., 2005), diffusion and biofilm processes (Kadlec and Knight, 1996; Polprasert et al., 1998; McBride and Tanner, 2000; Langergraber, 2003), or rate retardation (Shepherd et al., 2001), have been proposed for predicting CW behavior. While many of these models offer conceptually superior alternatives and underscore the lack of an accepted standard model, the simple (k) and modified (k–C^*) first-order models are the most widely used for predicting wetland performance (IWA, 2000; USEPA, 2000). Regardless of the model chosen, the complexity of constructed wetland biogeochemistry, the large range in influent OM concentration between systems and over time, and variation in OM measurement technique (e.g. TOC, BOD_5, COD) make generalizations from field data difficult and impede efforts to elucidate controls of treatment kinetics.

Understanding of the effects of temperature on constructed wetland performance and model constants has evolved considerably over the last two decades. Most design manuals have transferred standard wastewater treatment models based on microbial process kinetics to CWs. These models assume a positive relationship between temperature and the rate constant k, and hence CW performance for OM degradation (USEPA, 1988; WPCF, 1990; Reed et al., 1995). Some studies support this assumption (Reed and Brown, 1995; Griffin et al., 1999), but many others do not (e.g. Bavor et al., 1989; Gumbricht, 1992; Jenssen et al., 1994). Based on available data, Kadlec and Knight (1996) concluded that there was little, if any, influence of temperature on k. Kadlec and Reddy (2001), in a review of temperature effects in treatment wetlands, concluded that if any relation exists, it is negative, i.e. the rate constant for OM degradation decreases as temperature increases. Virtually no published information exists on the possible influence of temperature on residual OM represented by the C^* parameter.

Modeling of temperature responses is complicated by possible differences among plant species. Allen et al. (2002) and Hook et al. (2003) found that the effect of temperature on COD removal in subsurface wetlands was modified by presence and type of plant. The relationship between temperature and COD removal was strongly positive in unplanted wetland microcosms, positive but weaker in microcosms planted with *Typha latifolia*, neutral with *Schoenoplectus acutus*, and negative with *Carex utriculata*.[1] Differences in COD removal were associated with species-specific seasonal changes in indicators of root-zone oxidation.

In this paper, we use data from the microcosm studies reported by Allen et al. (2002) and Hook et al. (2003) to estimate parameters of the modified first-order k–C^* model for COD removal in constructed wetlands and to quantify the influence of temperature and plant species. The data set includes 192 time series of COD concentrations measured during batch incubations conducted under controlled greenhouse conditions. Collectively,

[1] In our previous publications, *C. utriculata* was listed as *C. rostrata* and *S. acutus* was listed as *Scirpus acutus*. Current taxonomy reclassifies most North American material labeled *Carex rostrata* as *C. utriculata* and all *Scirpus acutus*, globally, as *Schoenoplectus acutus* (USDA, NRCS. 2004. The PLANTS Database, Version 3.5 (http://plants.usda.gov). National Plant Data Center, Baton Rouge, LA 70874-4490, USA).

the data represent four plant treatments with four replicate microcosms each and 12 incubation periods at temperatures from 4 to 24 °C. Previously we used selected data from these experiments (incubation time-series at 4 and 24 °C in Allen et al. (2002); data for day 6 of 12 incubations conducted over 1 year in Hook et al. (2003)) to demonstrate seasonal and plant effects on COD removal and to develop an interpretation centered on plant-mediated oxygen transfer. In this study, we analyzed the entire data set in two stages. First, we used non-linear mixed effects regression (NLME) to fit the k–C^* model to all time series within each incubation period. Next, we evaluated the effects of temperature by fitting Arrhenius relationships to the k and C^* values for each plant treatment. Well-controlled experimental conditions eliminated many of the potential confounding factors that typically affect field data, such as precipitation and evapotranspiration, erratic temperatures, variation in influent mass loading or concentration, and non-ideal hydraulic influences on residence time (Kadlec and Knight, 1996; Kadlec, 2000). Water levels, influent wastewater composition, and loading rates were uniform across incubations, and temperatures were controlled during each incubation period. Consequently, these data provide a unique opportunity to model the combined influence of temperature and plants on COD removal.

2. Governing equations

The modified first-order k–C^* model proposed by Kadlec and Knight (1996) assumes that the volumetric COD removal rate is given by

$$R = k(C - C^*) \tag{1}$$

where C is the COD concentration (mg L^{-1}), C^* the residual COD concentration (mg L^{-1}), k the COD volumetric removal rate constant (day^{-1}), and R the COD volumetric removal rate (mg L^{-1} day^{-1}).

For batch-loaded systems, a material balance with Eq. (1) describing removal results in

$$\frac{C - C^*}{C_0 - C^*} = e^{-kt} \tag{2}$$

where C_0 is the initial COD concentration (mg L^{-1}), and t the treatment time (day).

Temperature effects on the removal rate constant are often accounted for by the Arrhenius relationship

$$k_T = k_R \theta^{T - T_R} \tag{3}$$

where k_T is the rate constant at a specified temperature T (day^{-1}), k_R the rate constant at a reference temperature T_R (day^{-1}), T the temperature (°C), T_R the reference temperature (°C), and θ the dimensionless temperature coefficient

Values of k_R (typically as k_{20}) and θ for constructed wetlands vary widely in published reports compared to values from other wastewater treatment systems. For subsurface flow (SSF) systems, USEPA (1988) suggested that BOD_5 k_{20} ranged from 0.86 to 1.84 day^{-1}, depending on media size, and that $\theta = 1.1$. Reed et al. (1995) suggested that $k_{20} = 1.104\ day^{-1}$ and $\theta = 1.06$. Kadlec and Knight (1996) reported $0.30 \leq k_{20} \leq 6.11\ day^{-1}$ with a weighted mean of 1.96 for subsurface systems. For surface flow wetlands Kadlec and Reddy (2001) suggested $0.900 \leq \theta \leq 1.015$ with an average of 0.983. Provided that C^* is constant across temperatures, values of θ greater than unity indicate a positive relationship between temperature and OM removal, while values less than unity indicate that the removal rate increases as temperature decreases.

Very little information exists on suitable values for C^*, and none seems to be available for the possible influence of temperature and season on this parameter. Kadlec and Knight (1996) suggested $1.7 \leq C^* \leq 18.2\ mg\ L^{-1}$ BOD_5 with a mean of 9.9. It is reasonable to expect a higher value of C^* if COD is the measure of OM because COD includes OM that would be considered recalcitrant in a BOD_5 test. Shepherd et al. (2001) report $23 \leq C^* \leq 450\ mg\ L^{-1}$ COD in wetlands treating winery wastewater.

3. Methods and materials

This study utilized 16 subsurface constructed wetland microcosms ("columns") housed in a greenhouse at Montana State University (45°40′N, 111°03′W, 1490 m elevation). Four columns each were planted with *C. utriculata* (Northwest Territory sedge), *S. acutus* (hardstem bulrush) and *T. latifolia* (broadleaf cattail), while four were left unplanted as controls. The

columns were constructed from 60 cm tall × 20 cm diameter polyvinyl chloride (PVC) pipe and filled to a 50 cm depth with washed, non-calcareous alluvial gravel (0.3–1.3 cm). Solution sampling tubes (0.3 cm diameter vinyl tubing) were installed from above with openings at depths of 5, 15, and 30 cm. Details of column design, construction and planting are fully described in Allen et al. (2002) and Hook et al. (2003).

A series of 20-day batch incubations were conducted on approximately monthly intervals between October 1997 and July 1999. Seasonal cycles of plant dormancy and growth were induced by varying the greenhouse set temperature between 4 and 24 °C, in 4 °C steps, in conjunction with the natural annual cycle of sunlight and day length. Though actual temperatures showed some diurnal and spatial variability, set temperatures represented average daily greenhouse and pore water temperatures. This paper utilizes data collected from the last 12 incubations, representing one annual cycle from August 1998 through July 1999. At the beginning of this period the system had been planted for 16 months and had been receiving wastewater for 11 months.

A synthetic wastewater formulation simulating secondary domestic wastewater was mixed from sucrose, hydrolyzed meat protein and inorganic and nutrient salts (Biederman, 1999). Mean influent concentrations of the main constituents were 470 mg L^{-1} COD, 44 mg L^{-1} N (27 amino N, 17 NH_4-N), 8 mg L^{-1} PO_4-P and 14 mg L^{-1} SO_4-S. Columns were gravity drained 3 days prior to each incubation and then again at the start of each incubation. Upon each emptying, columns were refilled from above with new synthetic wastewater. Water lost to evaporation was automatically replaced with tap water. Solution samples were drawn with a 60 mL syringe after three sample tube volumes (approximately 25 mL) had been withdrawn and discarded. No vertical gradients were evident in early incubations (Allen et al., 2002) so samples were taken from the 15 cm depth only. Sampling from all 16 columns occurred at days 0 (within 1 h after filling), 1, 3, 6, 9, 14 and 20 of each incubation. Duplicate samples were also drawn from influent water immediately before filling columns. Sub-samples were immediately analyzed for COD using colorimetric procedures (0–1500 mg L^{-1} Hach Corp., Loveland, CO) while other sub-samples were filtered, stored, and analyzed for other constituents reported elsewhere (Allen et al., 2002; Hook et al., 2003).

The parameters C_0, C^* and k of the modified first-order k–C^* model (Eq. (2)) were fit to the time series COD data using the S-PLUS statistical package (Insightful Corp., Seattle, WA, USA). Modeling was accomplished using a forward stepwise approach to non-linear mixed-effects regression (NLME). By using mixed effects, we allow each column to have its own (random) parameters (Lindstrom and Bates, 1990). Each of the 12 incubations was modeled separately. Parameter estimates were judged to have converged when improvement in likelihood was less than 10^{-06}. To analyze the effect of species, models were generated both with and without plant treatment effects. First, best-fit estimates were obtained for each of the parameters (C_0, C^* and k) across all columns, treating the 16 columns as replicates from the same population. Next, a species effect for each parameter was included. Within each incubation, the species effect was considered significant if the overall model fit was significantly improved (at $\alpha = 0.05$) by accounting for plant treatment. These NLME analyses tested the joint species effect on all three model parameters as a goodness of fit test. Variation in values of the individual parameters with respect to season and plant treatment was evaluated using repeated measures analysis of variance (ANOVAR).

Though our influent COD concentrations were relatively uniform, we let the NLME model fit the parameter C_0 rather than treating it as constant and equating it to either the average influent COD concentration or to the average COD concentration measured immediately after filling columns (day 0). We estimated C_0 statistically for two reasons. First, both influent and day 0 data were sampled values and therefore had random error associated with them, so neither could be considered an absolute initial value through which to force a model fit. Second, it was clear that there was substantial removal of COD almost immediately upon filling the columns. It appeared that this initial removal might be affected by plant treatment and temperature, so we considered it appropriate to treat the day 0 data as part of each time series and allow the model to fit C_0 as a parameter.

The Arrhenius relationship (Eq. (3)) was used to characterize the temperature dependence of k, C^*, and C_0 separately for each plant treatment. The NLME

regression analyses generated 192 estimates of each of the model parameters k, C^*, and C_0 as four estimates for each plant treatment and incubation (one per column, as described above). Temperature coefficients (θ_k, θ_{C^*}, and θ_{C_0}) and reference values (k_{20}, C^*_{20}, and $C_{0\text{–}20}$) were estimated from these parameters using regression analysis. Eq. (3) and equivalent equations for C^* and C_0 were log-transformed to linear form:

$$\ln(k_T) = \ln(k_{20}) + \ln(\theta_k)(T - 20) \quad (4)$$

Log-transformed parameter values for each column and temperature were regressed against relative temperature ($T - 20$), and the resulting slope and intercept back-transformed to estimate Arrhenius model constants. Because there were two incubations for each temperature setting (e.g. autumn versus spring, first versus second summer), eight estimates of k and C^* were available for each species–temperature combination; parameter values at each temperature were lumped, ignoring any seasonal hysteresis.

4. Results

The k–C^* model generally represented individual COD times series well (median coefficient of determination for regression $R^2 = 0.93$). Average goodness of fit was high ($R^2 > 0.80$) for all planted treatments at all temperatures and for unplanted controls at 16–24 °C; average fit was somewhat poorer for controls at 4–12 °C ($0.62 < R^2 < 0.79$). Representative incubations shown in Fig. 1 illustrate typical observed and modeled COD dynamics. Across temperatures and treatments, COD declined rapidly in days 1–3 and approached residual levels (C^*) by days 3–14. Sometimes COD values approached C^* within 1 day. At the highest temperatures, early rates of COD decline differed among plant treatments but C^* varied little. At the lowest temperatures, large differences in COD developed within the first day and persisted throughout incubations, resulting in large differences in C^* among plant treatments. While model fits were generally good, the rapid initial fall and the long, flat tail of the "L"-shaped curves often underestimated day 3 or 6 COD and overestimated days 9–20 COD slightly.

Average model parameters for each plant treatment and incubation are listed in Table 1. Values for the

Table 1
Mean values of parameters for the k–C^* model developed using the NLME technique[a]

Incubation	Temperature (°C)	*Carex*			*Schoenoplectus*			*Typha*			Control			Treatment p-value
		C_0 (mg L^{-1})	C^* (mg L^{-1})	k (day^{-1})	C_0 (mg L^{-1})	C^* (mg L^{-1})	k (day^{-1})	C_0 (mg L^{-1})	C^* (mg L^{-1})	k (day^{-1})	C_0 (mg L^{-1})	C^* (mg L^{-1})	k (day^{-1})	
10	24	426	48	0.60	401	40	0.48	398	76	0.39	415	109	0.89	0.1208
11	20	414	29	0.80	378	38	0.56	385	72	0.46	367	65	0.33	0.0004
12	16	407	25	1.23	413	30	0.64	388	57	0.31	360	58	0.16	0.0000
13	12	424	34	1.05	422	41	0.88	403	85	0.34	445	195	1.33	0.0000
14	8	383	30	1.82	372	50	0.70	392	113	1.12	388	206	1.06	0.0000
15	4	364	27	2.21	368	46	1.67	392	134	1.55	373	199	1.46	0.0000
16	4	316	35	2.28	334	52	1.62	381	168	2.49	347	230	2.07	0.0000
17	8	427	37	2.65	415	48	1.60	428	157	1.87	430	180	1.79	0.0002
18	12	371	41	1.31	366	80	2.06	394	103	0.89	341	53	0.17	0.0000
19	16	390	41	1.09	381	73	0.99	374	63	0.67	360	63	0.27	0.0014
20	20	421	60	1.33	400	39	0.86	400	48	0.88	378	58	0.34	0.0237
21	24	409	56	1.03	377	59	0.95	398	70	1.61	376	53	0.63	0.4080

[a] Each value is the mean of the four parameter estimates developed by individually fitting the k–C^* model to time series of measured COD concentrations from four replicate columns per plant treatment.

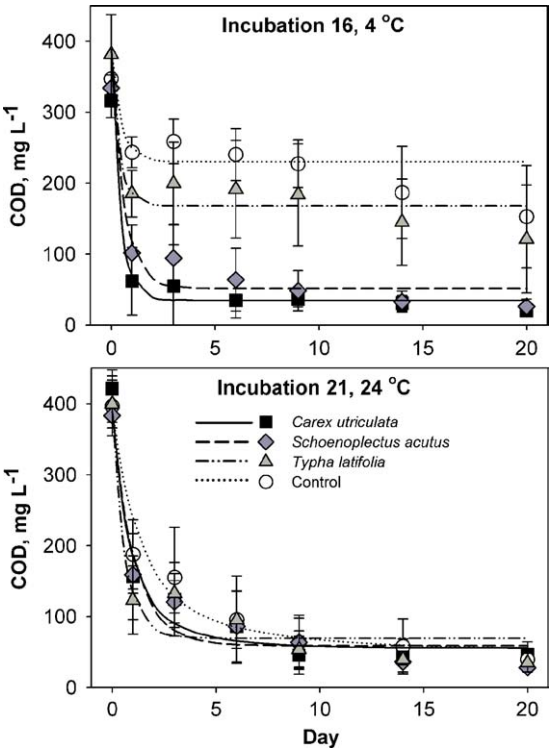

Fig. 1. Representative examples of COD dynamics during batch incubations at low and high temperatures. Symbols are means (±S.D.) of four replicates for each plant treatment. Lines are k–C^* model curves generated using the average values of k and C^* for each plant treatment.

rate parameter k are within ranges previously reported (Kadlec and Knight, 1996; Shepherd et al., 2001). Values for C^* are higher than values suggested by Kadlec and Knight (1996) using BOD_5 and are generally lower than those reported by Shepherd et al. (2001) measuring COD of winery waste. Intermediate values seem reasonable because we used COD rather than BOD_5 as a measure of organic matter removal, but used a relatively labile OM. The presence and species of plants had a significant effect ($\alpha = 0.05$) on model parameters for all but the warmest (24 °C) temperature setting. The p-values shown represent the significance of the plant treatment effect on the overall k–C^* model fit (i.e. fit to data was improved significantly by accounting for plant species), not tests for individual parameters.

Values of C_0 varied only slightly and showed no consistent differences among treatments or temperatures. Values of C_0 were generally lower at 4 °C than other temperatures; otherwise, variation was not clearly related to temperature as $\theta_{C_{0-20}}$ values were very near unity (Table 2). Although C_0 was estimated for individual time series during model fitting, this had few effects on COD predictions, and these were limited mostly to the first day; after day 1, differences between estimates that used the best-fit C_0 values shown in Table 1 and estimates that used a single, average C_0 value (389 mg L^{-1}) were <10 mg L^{-1}. Therefore, C_0 can reasonably be ignored in the analysis of k and C^*.

Averaged across seasonal incubations, the rate constant k was significantly greater for *Carex* than other treatments (ANOVAR $p < 0.001$), the residual C^* concentration was smaller for *Carex* and *Schoenoplectus* than for controls and *Typha* ($p < 0.001$), and initial C_0 concentration did not differ among treatments ($p = 0.48$). Rate constants showed strong seasonal variation within all treatments. Seasonal variation in residual COD levels (C^*) was strong in control and *Typha* columns but minimal for *Carex* and *Schoenoplectus*.

Fig. 2 compares mean measured COD concentrations at residence times of 1, 6 and 20 days to those predicted by the k–C^* model using mean parameter estimates shown in Table 1. Modeled estimates described overall seasonal patterns and plant species differences well but deviated from observed values systematically in some cases. Estimates and data agreed quite closely for *Carex* and *Schoenoplectus* across seasons and residence times. Models tended to underestimate day 6 COD (overestimate removal) and overestimate day 20 COD (underestimate removal) for *Typha* and controls, primarily at lower temperatures;

Table 2
Summary of temperature effects on parameters of the k–C^* model using an Arrhenius relationship

	k_{20} (day^{-1})	θ_k	C^*_{20} (mg L^{-1})	θ_{C^*}	C_{0-20} (mg L^{-1})	θ_{C_0}
Carex	0.925	0.945	42	1.029	414	1.008
Schoenoplectus	0.743	0.957	46	0.999	393	1.004
Typha	0.612	0.953	66	0.958	394	0.998
Control	0.366	0.936	67	0.935	383	1.003

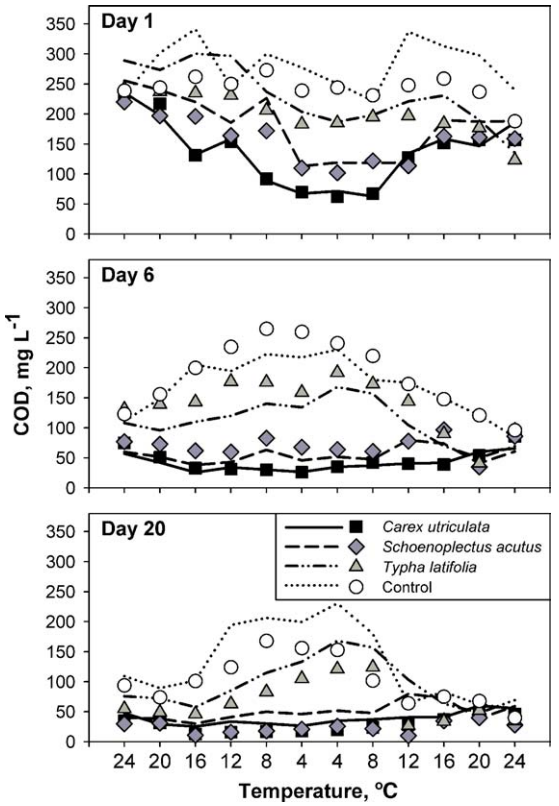

Fig. 2. Seasonal COD removal patterns on days 1, 6, and 20 of batch incubations as influenced by plant treatment and temperature. The sequence of temperatures on the abscissa corresponds to 20-day incubations conducted approximately monthly from 4 August 1998 through 4 August 1999. Symbols and lines represent means of observed and predicted COD concentrations, respectively. Predictions are based on average k–C^* model parameters shown in Table 1.

at 4–12 °C, errors averaged <40 mg L^{-1} for day 6 and <50 mg L^{-1} for day 20. Modeled patterns for day 6 agreed with those identified by Hook et al. (2003) based on repeated measures ANOVA analysis of the raw data; controls, and to a slightly lesser extent *Typha* columns demonstrated increased COD removal as temperature increased, while *Schoenoplectus* showed little temperature response and *Carex* had slightly lower removal as temperature increased. The qualitative agreement among raw data, conventional ANOVA analysis, and k–C^* model predictions suggests that the k–C^* model can account for relatively fine differences in performance if appropriately calibrated.

Fig. 3 plots estimates of the parameters k and C^* for individual columns against temperature. Lines represent unique Arrhenius relationships (Eq. (3)) for each plant treatment; corresponding constants are reported in Table 2. In all cases k declined with increasing temperature ($\theta_k < 1.0$) consistent with the conclusion of Kadlec and Reddy (2001) based on field data. Values of θ_k were similar among treatments (0.94–0.96). Values of k_{20} varied greatly from 0.93 to 0.37 day^{-1} and followed the same trend as overall performance with *Carex* > *Schoenoplectus* > *Typha* > unplanted controls. With the exception of *Carex* ($R^2 = 0.69$), Arrhenius relationships were not tightly determined by data ($0.37 < R^2 < 0.41$) due to substantial scatter in parameter values for individual time series. While some of this scatter was random, much of the variability for individual columns at a given temperature was due to seasonal hysteresis, with k values typically higher for spring than autumn incubations at the same temperature. Hysteresis was strongest for *Typha* and *Schoenoplectus*.

Temperature responses of C^* were more varied than those of k (Fig. 3). Values of θ_{C^*} ranged widely from 0.94 to 1.03, reflecting strongly negative relationships for controls and *Typha* and neutral or weakly positive relationships for *Schoenoplectus* and *Carex*. Values for θ_{C^*} were consistent with variation in seasonal performance with *Carex* > *Schoenoplectus* > *Typha* > unplanted controls. Values of C^*_{20} were slightly lower for *Carex* and *Schoenoplectus* than for *Typha* and unplanted controls. In planted columns, C^* values suggested slight seasonal hysteresis, with values typically higher in spring than autumn.

The net effects of temperature on predicted COD dynamics are shown in Fig. 4. Lines represent COD concentrations predicted by the k–C^* model when values of k and C^* were calculated from the Arrhenius relationships provided in Table 2 and Fig. 3. Predictions matched observations reasonably well for all treatments on days 1 and 20, and for *Schoenoplectus* and *Carex* on day 6. However, predictions generally underestimated COD (i.e. overestimated COD removal) for *Typha* and controls on day 6. Both modeled and observed COD patterns illustrate that the effect of temperature differed among plant treatments and varied with residence time. With *Carex* and *Schoenoplectus*, day 1 COD removal improved as temperature *decreased*; by day 6, temperature effects were weak or absent. With *Typha* and unplanted controls, day 1 COD removal was essentially unaffected by tempera-

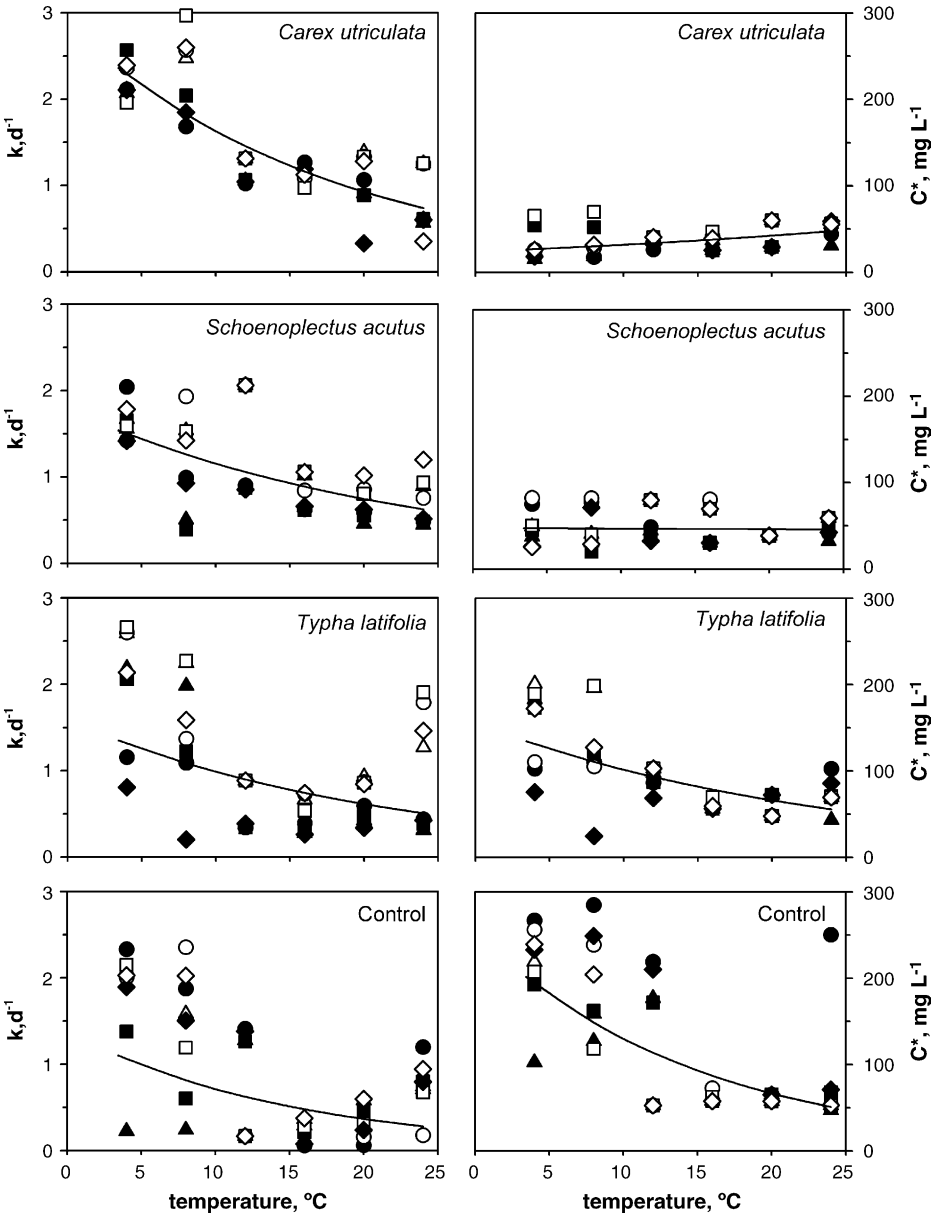

Fig. 3. Relationships between temperature and k–C^* model parameters. Each symbol represents the parameter value estimated from an individual column's time series. At a given temperature, filled symbols represent the first six incubations (summer–autumn–winter descending temperature sequence) and empty symbols represent the remaining incubations (winter–spring–summer ascending temperature sequence). Lines represent best-fit, Arrhenius relationships (parameters reported in Table 2).

ture; by day 6, COD removal improved as temperature *increased*. Across all residence times, differences in species performance were greater at lower temperatures. At low temperatures, differences in performance during early stages of incubations were associated with differences in both k and C^*, while performance differences at later stages were related mainly to differences in C^* (Figs. 1 and 4).

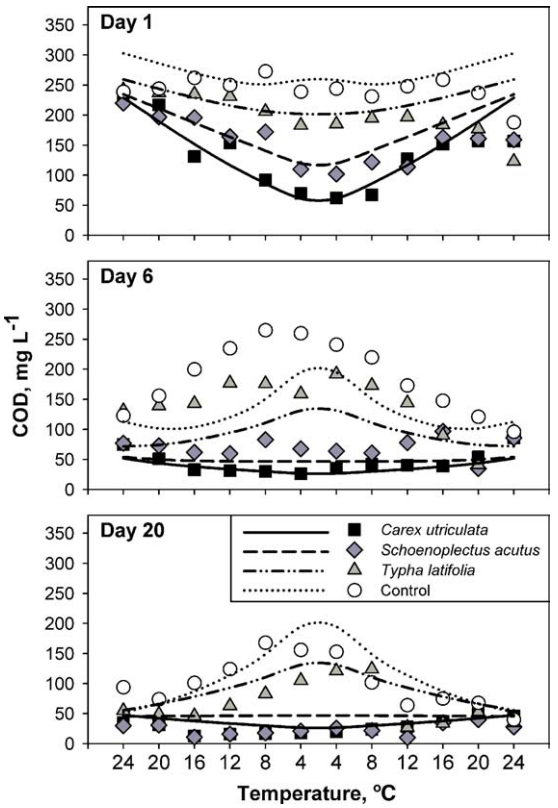

Fig. 4. Seasonal COD removal patterns observed on days 1, 6, and 20 of batch incubations (symbols) and modeled using k and C^* values predicted using the Arrhenius relationships shown in Table 2 and Fig. 3 (lines). Symbols and abscissa are as described for Fig. 2.

5. Discussion

Arrhenius relationships representing the temperature dependence of k and C^* successfully captured the main seasonal patterns in observed data; i.e. COD removal rates varied strongly with temperature, temperature-dependence was modified dramatically by presence and species of plants and varied with residence time, and net differences in performance among species were greatest at lower temperatures. Overall performance for COD removal was ranked, from best to worst, *Carex* > *Schoenoplectus* > *Typha* > control, with greatest differences at lower temperatures as reported previously (Allen et al., 2002; Hook et al., 2003) and at shorter residence times. The current analysis indicated that species effects were significant at all but the highest temperature evaluated (24 °C).

Species effects on performance were largely a result of differences in temperature responses. In *Carex* and *Schoenoplectus* columns, low temperatures enhanced early COD removal rates but had negligible effects at intermediate and long residence times. In contrast, low temperatures in *Typha* and control columns had slight effects on early COD removal but reduced removal at intermediate and long residence times. As would be expected from these patterns, variations in both k and C^* were important in modeling temperature and plant effects on performance. Temperature responses correlated mainly with variation in k at short residence times (through days 1–3 depending on plant treatment), and with variation in C^* at longer residence times ($\geq$6 days). Plant species differences correlated mainly with variation in k at warmer temperatures and shorter residence times, and with variation in C^* at colder temperatures and longer residence times.

The role of C^* in performance variation is striking. Poor low-temperature COD removal in *Typha* and control columns was mainly due to relatively high residual concentrations compared to warmer temperatures. Residual COD responded little to temperature in *Carex* and *Schoenoplectus* columns. At the lowest temperature, average C^* values were seven times higher for controls than for *Carex* columns, corresponding to 54% versus 94% COD removal. At the highest temperature, C^* values were uniformly low, resulting in 80–90% COD removal for all treatments. Values of k increased with decreasing temperatures in *Typha* and control treatments, and thus were not responsible for lowered removals. Because variation in the rate constant alone cannot explain the observed differences due to species, temperature and residence times, our results support the contention of others (e.g. Kadlec and Knight, 1996; Shepherd et al., 2001) that the k–C^* model is superior to the simple first-order model.

We agree with Kadlec (2000) that the k–C^* model is not phenomenologically based but is rather an empirical improvement over the simple first-order model. Nevertheless, variations in parameter magnitudes, especially C^*, do appear to have a phenomenological basis. Our methods eliminated many of the sources of variability that confound estimates of residual COD (Kadlec, 2000); therefore, our C^* values may provide a more accurate window into the influence of temperature, season and plant species on it. We did not evaluate the cause of differences in residual COD

concentrations, but we speculate that they reflect differences in the daughter products of microbial utilization of influent OM.

Uniform, synthetic wastewater containing highly labile OM was used throughout our study, but the size of the relatively persistent pool represented by C^* varied markedly, thus our C^* values were not a weak function of influent OM concentration as proposed by Kadlec and Knight (1996) and Kadlec (2000). The fact that C^* varied most in unplanted controls and was virtually constant in two of the planted treatments argues strongly for a microbial rather than a plant source for the residual COD. It appears that at low temperatures microbial degradation was less efficient and/or yielded more recalcitrant degradation products in *Typha* and control columns than when *Carex* or *Schoenoplectus* was present. This may have resulted from the strongly anaerobic conditions that prevailed throughout the year in *Typha* and control columns and which contrasted with the weakly anaerobic to moderately oxidized conditions that developed during colder months in *Carex* and *Schoenoplectus* columns (Allen et al., 2002; Hook et al., 2003). Differences in redox conditions likely influenced the metabolic pathways involved in organic matter removal (Kadlec and Reddy, 2001; Stein and Hook, 2005) and perhaps the quantity of microbial products recalcitrant within the 20-day batch.

Though the k–C^* model fit individual COD time series well and adequately described effects of temperature and plant species on COD removal when combined with Arrhenius relationships for individual model parameters, several aspects of model behavior potentially affect its application to CW design and research. Observed COD time series suggest existence of an almost instantaneous removal mechanism, possibly sorption as postulated by McBride and Tanner (2000), that is not explicitly represented in the k–C^* model. More importantly, interactions between k and C^*, and between θ_k and θ_{C^*}, complicate interpretation the effects of individual parameter values on COD removal and may be influenced by the statistical procedures used to calibrate them.

Our good k–C^* model fits were obtained by using initial COD values that were substantially lower than measured influent concentrations, i.e. by fitting C_0 to data. Concentrations measured within 1 h after adding wastewater to columns showed that 2–25% of influent COD (approximately 15% on average) was immediately removed from solution. Riley et al. (2005) observed similar rapid removal of ammonium and used in vitro tests to demonstrate that gravel sampled from *Carex* columns had a high sorptive capacity. We hypothesize that the rapid initial removal of COD involves sorption on biofilms, and that batch operation (versus continuous flow) may rejuvenate sorption sites by periodically oxidizing sorbed OM (Riley et al., 2005; Stein et al., 2003). Neither the basic first-order model nor the modified k–C^* model accounts for such an initial removal mechanism. We partially accounted for it by including day 0 values and allowing C_0 to be fit by the model, but because all model parameters were optimized jointly, estimates of C_0 reflect the influence of the entire COD time series on overall model fit. Nonetheless, most measured day 0 COD and statistically estimated C_0 values agreed well. In the future, it may be appropriate to add an initial sequestration or sorption term to COD removal models and use the measured influent concentration as the starting concentration. However, proper calibration of initial removal rates would require intensive sampling at very short residence times.

Statistically, k and C^* are not independent, either when fitting individual time series or when evaluating temperature and species effects. The mathematical interaction of k and C^* is clear in Eqs. (1) and (2); relative changes in rate through time are dictated by k, but actual removal rates are scaled to the difference between C_0 and C^*. Temperature responses of k and C^* can be independent only if one parameter is relatively constant across temperatures. Because C^* varied little with temperature for *Carex* and *Schoenoplectus* (Fig. 3), k and C^* were independent or weakly correlated ($r = -0.17$ and 0.52, respectively), but because both varied for *Typha* and controls, correlation was relatively strong ($r = 0.79$ and 0.89, respectively). Because k is not independent from C^* in the k–C^* model, the temperature response of COD removal is determined by both θ_k and θ_{C^*}, not by θ_k alone. Therefore, values of θ_k greater than one do not necessarily indicate a positive relationship between temperature and OM removal, nor do values less than one necessarily indicate a negative relationship. Although the rate constant increased with a decrease in temperature for all species, only *Carex* and *Schoenoplectus* showed improved performance at colder temperatures; this was seen at all residence times with *Carex* and through day 3 with

Schoenoplectus. *Typha* and control performance never benefited from low temperatures. Overall performance differences and their amplification at lower temperatures were more closely related to k_{20} and θ_{C^*} than to θ_k and C^*_{20}. Like COD removal, k_{20} and θ_{C^*} ranked *Carex* > *Schoenoplectus* > *Typha* > control (Table 2).

The interaction of k and C^* can result in unexpected predictions of COD response to temperature. For example, predicted COD removal can be greatest (or poorest) at intermediate temperatures, following twice-yearly oscillations rather than a consistent annual cycle (there is a trace of this in the mild hump in the day 1 control curve in Fig. 4). This phenomena can occur only when both θ_k and θ_{C^*} are less (or greater) than unity (as seen for *Typha* and controls in Fig. 3), such that the effects of temperature on k and C^* oppose each other in terms of COD removal. This potential behavior is inherent to the form of the k–C^* model rather than the use of the Arrhenius relationship for temperature effects. Even if one assumes k and C^* are independent conceptually (if both are influenced by microbial responses to changes in the wetland environment as we hypothesize, they are not independent), there are interactions when statistically optimizing the parameters.

Our optimized model parameters failed to describe the ongoing, gradual COD declines seen in later phases of many incubations. Rather C^* values tended to reflect the average COD concentrations over intermediate and longer residence times. Considering the typical "L" shape of k–C^* model curves, it is likely that sampling more or less intensively during early or later portions of incubations would affect k and C^* estimates. Small variations in optimized k and C^* values are magnified when these values are compared to temperature. Thus the sampling frequency, the statistical procedures used and/or the choice of goodness of model fit criteria might produce oscillations in predicted performance versus temperature even if oscillations are not expressed in the data. These statistical concerns suggest that future publications should provide more detail about the statistical methods used to estimate parameters.

From a practical perspective, we urge caution when applying our results to field conditions. Perhaps our most intriguing result is the strong interactions between temperature and plant species grown in monoculture. Operational CWs almost always contain a variety of species and each potentially has a unique seasonal variation on performance. Thus field performance may vary at least within the range observed in our study. If so, summer performance can be predicted by the k–C^* model with some reliability, while winter performance predictability may vary between excellent and poor.

6. Summary and conclusion

The modified k–C^* first-order model (Eq. (2)) proposed by Kadlec and Knight (1996) fit 192 COD time series measured in batch-loaded wetland microcosms reasonably well. NLME statistical modeling found a significant plant species effect at all but the warmest (24 °C) temperatures of the study. The effects of temperature on both the rate parameter k and the background COD concentration C^* tended to accentuate differences between plant treatments at colder temperatures and to minimize differences at warmer temperatures. Performance differences were associated mainly with k at short residence times and warm temperatures, and with variation in C^* at long residence times and cold temperatures. Estimates of the rate parameter k increased with decreasing temperature ($\theta_k < 1$) for all treatments, in contrast to conventional assumptions but in agreement which more recent analyses of the temperature dependence of OM degradation rates (e.g. Kadlec and Reddy, 2001). However, temperature responses of COD removal were not always consistent with temperature responses of k; the temperature response of C^* also affected performance and interacted with the effect of k. Overall species differences in performance and in temperature responses were associated mainly with differences in k_{20} and θ_{C^*} rather than θ_k. This modeling effort demonstrated the relative importance of C^* when using the k–C^* model. Unless a wetland is operated with a very short retention time, the rate parameter k may be less important than the residual concentration C^* when predicting effluent OM values. If most CWs are over-designed with respect to OM removal (Kadlec and Knight, 1996), effluent COD values will depend more upon C^* than k, emphasizing the need to understand the nature and behavior of residual COD.

Our analyses emphasize the need to focus modeling efforts on accurately representing the broad seasonal patterns of COD removal and the factors that control them. The choice of specific temperature-response models and parameter values is not dictated by data

from well-controlled experiments (this study) or operational CWs (Kadlec and Knight, 1996; Kadlec and Reddy, 2001). Random variation and complex biological cycles produce relatively "noisy" data with seasonal patterns, such as hysteresis, that are not directly correlated with temperature. Given the relatively loose relationships between temperature and COD removal, various models, including those used here, can undoubtedly achieve equally good fit to data. Model selection may then be based on considerations such as simplicity, adequacy, and vulnerability to unrealistic behavior.

Acknowledgements

We thank David Shanight and Kate Riley for many hours of sample collection and analysis. A large debt of appreciation also goes to Gael Decoudu for coding the NLME routines with the statistical package S+ and Jim Robison-Cox for suggesting the NLME routines and reviewing the manuscript. Funding was provided by: USDA-NRI Competitive Grants Program, Award 96-35102-3837; Bureau of Reclamation, Agreement 97-FG-60-09030; Montana University Water Resources Center and the USGS Water Resource Research Program; US EPA Science to Achieve Results (STAR) Fellowship Program; and Montana Agricultural Experiment Station, Projects MONB00127 and MONB00199 (Journal Series No. 2002-21). The support of NIWA, the National Institute of Water and Atmospheric Research, Ltd, New Zealand during the writing of this manuscript is also greatly appreciated.

References

Allen, W.C., Hook, P.B., Biederman, J.A., Stein, O.R., 2002. Temperature and plant species effects on wastewater treatment and root-zone oxidation in wetland microcosms. J. Environ. Qual. 31 (3), 1010–1016.

Bavor, H.J., Roser, D.J., Smalls, I.I., 1989. Performance of solid-matrix wetland systems viewed as fixed film reactors. In: Hammer, D.A. (Ed.), Constructed Wetlands for Wastewater Treatment. Lewis Publishers, Chelsea, MI, pp. 646–656.

Biederman, J.A., 1999. Temperature and Plant Effects on Secondary Wastewater Treatment in Model Constructed Wetlands. M.S. Thesis. Montana State University, Bozeman, MT.

Griffin Jr., D.M., Bhattarai, R.R., Xiang, H., 1999. The effect of temperature on biochemical oxygen demand removal in a subsurface flow wetland. Water Environ. Res. 71 (4), 476–482.

Gumbricht, T., 1992. Tertiary wastewater treatment using the root zone method in temperate climates. Ecol. Eng. 1, 199–212.

Hook, P.B., Stein, O.R., Allen, W.C., Biederman, J.A., 2003. Plant species effects on seasonal performance patterns in model subsurface wetlands. In: Mander, Ü., Jenssen, P.D. (Eds.), Constructed Wetlands for Wastewater Treatment in Cold Climate Areas. WIT Press, Ashurst, UK, pp. 87–106.

IWA, 2000. Constructed Wetlands for Pollution Control: Processes, Performance, Design, and Operation. Scientific and Technical Report No. 8. IWA Publishing, London, UK.

Jenssen, P.D., Maehlum, T., Krogstad, T., 1994. Adapting constructed wetlands for wastewater treatment in northern environments. In: Mitsch, W. (Ed.), Global Wetlands: Old World and New. Elsevier, New York, NY.

Kadlec, R.H., 2000. The inadequacy of first-order treatment wetland models. Ecol. Eng. 15, 105–119.

Kadlec, R.H., Knight, R.L., 1996. Treatment Wetlands. Lewis Publishers, Boca Raton, FL.

Kadlec, R.H., Reddy, K.R., 2001. Temperature effects in treatment wetlands. Water Environ. Res. 73 (5), 543–557.

Langergraber, G., 2003. Simulation of sub-surface flow constructed wetlands—results and further research needs. Water Sci. Technol. 48 (5), 157–166.

Lindstrom, M.J., Bates, D.M., 1990. Nonlinear mixed effects models for repeated measures data. Biometrics 46, 673–687.

McBride, G.B., Tanner, C.C., 2000. Modeling biofilm nitrogen transformations in constructed wetland mesocosms with fluctuating water levels. Ecol. Eng. 14, 93–106.

Mitchell, C., McNevin, D., 2001. Alternative analysis of BOD removal in subsurface flow constructed wetlands employing monod kinetics. Water Res. 35 (5), 1295–1303.

Polprasert, C., Khatiwada, N.R., Bhurtel, J., 1998. Design model for COD removal in constructed wetlands based on biofilm activity. ASCE J. Environ. Eng. 124 (9), 838–843.

Reed, S.C., Brown, D.S., 1995. Subsurface flow wetlands—a performance evaluation. Water Environ. Res. 67, 244–248.

Reed, S.C., Crites, R.W., Middlebrooks, E.E., 1995. Natural Systems for Waste Management, 2nd ed. McGraw-Hill, New York, NY.

Riley, K.A., Stein, O.R., Hook, P.B., 2005. Ammonium removal in constructed wetland microcosms as influenced by presence and species of plants and organic carbon load. J. Environ. Sci. Health, Part A 40 (6/7), 1109–1121.

Rousseau, D.P.L., Griffin, P., Vanrolleghem, P.A., DePauw, N., 2005. Model study of short-term dynamics of secondary treatment reed beds at Saxby (Leicestershire, UK). J. Environ. Sci. Health, Part A 40 (6/7), 1479–1492.

Shepherd, H.L., Tchobanoglous, G., Grismer, M.E., 2001. Time-dependent retardation model for chemical oxygen demand removal in a subsurface-flow constructed wetland for winery wastewater treatment. Water Environ. Res. 73 (5), 597–606.

Stein, O.R., Hook, P.B., Biederman, J.A., Allen, W.C., Borden, D.J., 2003. Does batch operation enhance oxidation in subsurface constructed wetlands? Water Sci. Technol. 48 (5), 149–156.

Stein, O.R., Hook, P.B., 2005. Temperature plants and oxygen: how does season affect constructed wetland performance? J. Environ. Sci. Health, Part A 40 (6/7), 1331–1342.

USEPA, 1988. Constructed Wetlands and Aquatic Plant systems for Municipal Wastewater Treatment. EPA/625/1-88/002. Center for Environmental Research Information, Cincinnati, OH.

USEPA, 2000. Constructed Wetlands Treatment of Municipal Wastewaters. EPA 625-R-99-010. National Risk Management Research Laboratory, Cincinnati, OH.

WPCF, 1990. Natural Systems For Wastewater Treatment. Manual of practice FD-16. In: Chair, S.C.R. (Ed.), Task Force on Natural Systems. Water Pollution Control Federation, Alexandria, VA.

Wynn, T.M., Liehr, S.K., 2001. Development of a constructed wetland subsurface-flow wetland simulation model. Ecol. Eng. 16, 519–536.