INFLUENCE OF POLLUTANT LOADING RATE ON SEASONAL PERFORMANCE OF MODEL CONSTRUCTED WETLANDS

by

Rickey Lynn Schultz Jr.

A thesis submitted in partial fulfillment
of the requirements for the degree of

of

Master of Science

in

Environmental Engineering

MONTANA STATE UNIVERSITY
Bozeman, Montana

November 2007

APPROVAL

of a thesis submitted by

Rickey Lynn Schultz Jr.

This thesis has been read by each member of the thesis committee and has been found to be satisfactory regarding content, English usage, format, citation, bibliographic style, and consistency, and is ready for submission to the Division of Graduate Education.

Dr. Otto Stein

Approved for the Department of Civil Engineering

Dr. Brett W. Gunnick

Approved for the Division of Graduate Education

Dr. Carl A. Fox

STATEMENT OF PERMISSION TO USE

Rickey Lynn Schultz Jr.

November 2007

ACKNOWLEDGEMENTS

I would like to extend much appreciation to my advisor Dr. Otto Stein for giving me the opportunity to further my education and live in such a beautiful part of the country. His support, guidance and friendship undoubtedly made this project interesting and worthwhile. I would also like to thank the other members of my committee Drs. Paul Hook and Warren Jones for their suggestions and patience throughout my studies. I must thank all the other individuals who made it possible for me to carry out this research. These include laboratory manager John Neuman, laboratory technician Wes Harms, and undergraduate assistants Jeff Barron, Ryan Wallace, and Melissa Schroeder. Finally I thank all my friends and family for their love and support.

This work is dedicated to Eva Schultz. Thanks for your humor and love.

TABLE OF CONTENTS

LIST OF TABLES

Table Page

LIST OF FIGURES

Figure Page

ABSTRACT

Constructed wetlands (CW) are a viable alternative wastewater treatment technology for many wastewater types. However, recommended loading rates vary widely between regulatory agencies. A greenhouse experiment was carried out for approximately 19 months to study the effect of loading rate, plant species selection, temperature and season on pollutant removal in bench-scale constructed wetlands. The wetlands were operated in batch mode at batch lengths of 3, 6, and 9 days, corresponding to loading rates of 210, 105, and 70 kg COD/ha•d, respectively. Greenhouse temperature cycled from 4°C to 24°C. Treatments included plant species *Carex utriculata*, *Schoenoplectus acutus* and *Typha latifolia* and unplanted controls. Water and air temperature, redox potential, COD, SO_4^{2-}, NH_4^+, PO_4^{3-} and pore volume were monitored throughout the study.

Data from the current research is compared with a previous study performed under similar conditions, but with a 20 day batch length resulting in a loading rate of 32 kg COD/ha•d. Performance of all treatments and loading rates was compared on the basis of percent COD and SO_4^{2-} removal, redox potential, and remaining NH_4^+ and PO_4^{3-} concentration. There were strong interactions between loading rate, plant species and temperature. Within species, pollutant removal typically decreased with an increase in loading rate at all temperatures. Planted treatments generally improved pollutant removal at all loading rates and typically removed more NH_4^+ and PO_4^{3-} at 24°C than at 4°C. However at lighter loading rates *Carex* and *Schoenoplectus* showed little temperature effect for COD removal, and had more SO_4^{2-} remaining and increased redox levels at 4°C. However, as loading rate increased these species tended to have poorer COD removal at colder than warm temperatures. These results indicate that the ability of some plant species to increase aerobic respiration due to increased oxygenation in winter, and thus mitigate typical temperature effects on COD removal, is limited by higher organic load rates.

Although not the focus of this study it was observed that wetland column porosity varied with season and with wetland age. Column porosity was lower for older columns and during winter.

INTRODUCTION

A single, satisfactory definition of “wetland” is difficult to ascertain. Generally speaking, a natural wetland can be considered a transitional ecosystem occurring between terrestrial and aquatic ecosystems that is periodically saturated with water as to create saturated soil conditions and support the prevalence of hydrophytes, or flooding tolerant plants (Mitsch and Gosselink, 1993). Discharge of wastewater into natural wetlands has occurred globally for centuries and early research conducted in the United States in the 1970’s involved the use of natural wetlands for treatment of wastewater. However, application of wastewater to natural wetlands typically changed their ecosystem value by altering species composition and community structure and function. Much of this work was inspired by earlier research on wetlands engineered specifically for water treatment conducted in Germany starting in the early 1950s by Dr. Seidel and later by Dr. Kickuth. Their systems eventually became known as constructed wetlands.

Constructed wetlands (CWs), also called treatment wetlands, are engineered natural treatment systems that mimic natural wetlands and remove waterborne pollutants through a combination of physical, chemical, and biological processes. Constructed wetlands may be used to treat a variety of polluted waters, including industrial and agricultural wastewaters, stormwater runoff, acid mine drainage, and polluted surface waters, but the majority of use has been for domestic or municipal wastewater (Kadlec and Knight, 1996).

Use and improvement of constructed wetlands technology grew rapidly after about 1980 when monitoring of natural wetlands revealed the system's effectiveness in treating wastewater and the advantages of constructing wetlands, or perhaps better stated as the lack of advantages in using natural wetlands, were realized. Additionally, the use of constructed over natural wetlands provided more control over treatment processes (Brix, 1994). Constructed wetlands are now widely recognized as a cost effective, low maintenance, sustainable treatment technology ideal for areas with low population densities and for developing countries. Worldwide there are over 50,000 wetland treatment systems in use today (WERF, 2006).

Two common types of constructed wetlands are free water surface (FWS) wetlands and subsurface-flow (SSF) wetlands. FWS wetlands resemble natural wetlands in that water, typically less than a 1 m deep, is exposed to the atmosphere and flows through the leaves and stems of emergent vegetation. Conversely, SSF wetlands, also called vegetated submerged bed (VSB) wetlands, do not have standing water and wastewater flows through the root zone of emergent vegetation in a media of rock or gravel. One practical advantage of SSF wetlands over FWS wetlands is the isolation of wastewater below ground, which reduces odor and the risk of the spread of disease. Additionally, in cold climate regions a layer of ice may form on open waters in

FWS wetlands (US EPA, 2000). Therefore, SSF wetlands are ideal for use in cold climate regions like Montana and are used in the current study.

Pollutant Loading Rate in SSF Wetlands

The design of constructed wetlands has largely been based on empirical methods resulting in variable treatment performance (Brix, 1994). One rational design criterion used by the United States Environmental Protection Agency (US EPA) and other entities to size constructed wetlands is pollutant loading rate and Kadlec and Knight (1996) state loading rate as an important factor in the design and operation of wetland treatment systems. Because the water level in subsurface wetlands is beneath a layer of plant detritus and gravel, transfer of atmospheric oxygen to the wetland matrix is limited. A limited oxygen supply inhibits aerobic decomposition of organic matter and transformation of nitrogen by nitrification. Pollutant removal can be optimized by balancing pollutant loading rate and oxygen transfer. If pollutant loading rate exceeds oxygen transfer rate then oxidation of pollutants is limited. This balance can be shifted in favor of pollutant removal by either decreasing loading rate or increasing oxygen supply (WERF, 2006).

Several design-oriented publications have recommended areal pollutant loading rates for subsurface constructed wetlands treating municipal primary or septic tank effluent. However, recommended loading rates range widely.

Varying hydraulic residence time is one method that can be used to change loading rate. For constructed wetlands operated in drain-fill or batch mode, batch length is equivalent to hydraulic residence time and is inversely proportional to loading rate. For an effluent with a maximum biological oxygen demand (BOD) of 30 mg/L the Tennessee Valley Authority (TVA, 1993) and United States Environmental Protection Agency (US EPA, 2000) recommend BOD loading rates of 53 kg/ha•d and 60 kg/ha•d, respectively. To produce the same effluent quality 50% of the time the Water Environment Research Foundation (WERF, 2006) suggests a BOD loading rate of 80 kg/ha•d, but to meet this standard 75% of the time, loading should be only 15 kg/ha•d. The range of these values indicates the inherent dynamics and variability in natural treatment systems, but also the need for better understanding of removal processes and improved design guidelines. More confidence in higher loading rates from additional research results in smaller wetland surface area, decreasing cost and increasing feasibility of usage.

There have been many investigations into the effect of pollutant loading on constructed wetland performance. Tanner et al. (1995a) varied loading rate by operating a group of planted and unplanted constructed wetlands at retention times between two and seven days, with resulting loading rates of 41 to 9 kg $CBOD_5$/ha•d, respectively. An increase in removal rate and decrease in percent removal of total BOD with increased loading rate in planted wetlands was observed. Percent removal of total BOD decreased from 80% at the lowest loading to 50% at the highest loading. Also, removal of total BOD was greater in planted wetlands than unplanted, with a greater effect at higher loadings. In a companion paper (Tanner et al. 1995b) which focused on nitrogen and phosphorus removal, similar results were noted. Removal rates for total nitrogen (TN) and total phosphorus (TP) increased with increased loading, while percent removal decreased. Also, planted wetlands showed greater TN and TP removal than unplanted wetlands, especially at higher loadings. Another interesting result was the decline in above-ground plant biomass with decreased loading rate. In a follow-up article (Tanner et al. 1998) that examined the mature planted wetlands' long-term performance, relatively constant BOD and TN removal was found. This was especially surprising because pore volume and therefore wetland retention time was decreased due to clogging. TP removal decreased by the fifth year of operation by about 20-40%, presumably due to saturation of sorption sites.

Jing et al. (2002) found similar effects of loading rate on constructed wetland treatment performance. A direct relationship between COD loading rate (60 – 150 kg/ha•d) and COD removal rate was found for wetlands operated with retention times between one and four days. All planted wetlands had >70% COD removal at a retention time of two days or greater. Highest removal efficiencies for nitrogen and phosphorus occurred with a retention time of three days. All results were for warm temperatures, 20 – 32°C. However, Akratos and

Tsihrintzis (2007) conducted a similar study investigating a broader range of temperatures (2 – 26°C) and much longer residence times are recommended. A residence time greater than eight days (loading rate < 35 kg BOD/ha•d) is recommended for at least a 90% reduction in BOD. Eight days was also sufficient to achieve high ammonia removal at temperatures greater than 15°C, but a residence time of at least 20 days was needed to achieve about 70% ammonia removal at temperatures less than 15°C. Recommended residence times based on phosphorus removal were similar to those based on nitrogen removal.

Batch Operation of SSF Wetlands

The aforementioned studies investigated wetlands operated in continuous flow mode only. SSF wetlands can also be operated in batch mode, also called drain-fill or tidal flow operation, where the wetland is filled with wastewater, remains for a given period of time, called a batch length, followed by a draining period. Discharging wastewater from a batch operated wetland acts like a passive air pump and promotes aeration of the wetland subsurface. The increased availability of oxygen in batch operated CWs allows for increased pollutant removal. Several researchers have noted the capacity of batch operated constructed wetlands to enhance pollutant removal (Busnardo et al., 1992; Tanner et al., 1999; Behrends et al., 2001; Stein et al., 2003; Sun et al., 2005), but at least one did not (Burgoon et al., 1995). Therefore, it has been suggested that wetlands operated in batch mode may perform better than wetlands operated in conventional continuous flow and might handle higher loading rates (US EPA, 2000; WERF, 2006). However, investigation into pollutant loading rate based on batch length for batch operated constructed wetlands is lacking, especially for cold climate regions.

Objectives and Approach

The objective of this research was to determine the influence of pollutant loading rate on seasonal performance of model subsurface constructed wetlands. Seasons were simulated by varying temperature between 4°C and 24°C over a 19 month greenhouse study. A synthetic wastewater was batch loaded into 32 subsurface wetlands in either three, six, or nine day batch lengths corresponding to loading rates of 210, 105, and 70 kg COD/ha•d, respectively. Performance was evaluated by measuring COD and sulfate removal, redox potential, and phosphate and ammonium concentration. Results from previous research (Allen et al., 2001, Hook et al., 2003) where 20 day batch lengths (32 kg/ha•d) were evaluated are incorporated and compared with the current loading rates. Results for all temperatures are presented and are statistically compared at the two temperature extremes, 4°C and 24°C. Pore volume was measured in model wetlands for approximately 24 months. Influence of system age and season on porosity are also briefly examined.

METHODS AND MATERIALS

Experimental Overview

Thirty-two subsurface flow constructed wetland microcosms ("columns") were batch-loaded with a synthetic wastewater in a controlled-temperature greenhouse at Montana State University-Bozeman. Greenhouse temperatures ranged from 4°C to 24°C (Figure 1) over ten 60-day constant temperature periods ("incubations"). Columns were separated into two groups of 16 columns. Each group contained four replicates each of three different planted treatments and unplanted controls. The plant species used were *Carex utriculata* (Northwest territory sedge), *Schoenoplectus acutus* (hardstem bulrush) and *Typha latifolia* (broadleaf cattail). Batch lengths of three, six , and nine days were used resulting in nominal organic loading rates of 210, 105, and 70 kg COD/ha•d, respectively. The effect of batch length, or conversely loading rate, on carbon, sulfate, redox potential, nitrogen and phosphate was assessed based on time series data collected during a 19 month experimental period. Data from the current research was compared to previous research where a 20 day batch length was used (32 kg COD/ha•d).

System Design and Construction

Columns were constructed and planted in April 1997 for an earlier research study. Each column was constructed from 60 cm tall x 20 cm diameter polyvinyl chloride (PVC) pipe and filled to a depth of 50 cm with washed, non-calcareous alluvial gravel (0.3 – 1.3 cm in diameter). Initial column porosity was 0.27 with a resulting pore volume of 4.3 L, which did not differ significantly among replicates (Allen, 1999). Details of earlier studies may be found in Biederman (1999), Allen et al. (2002), and Hook et al. (2003).

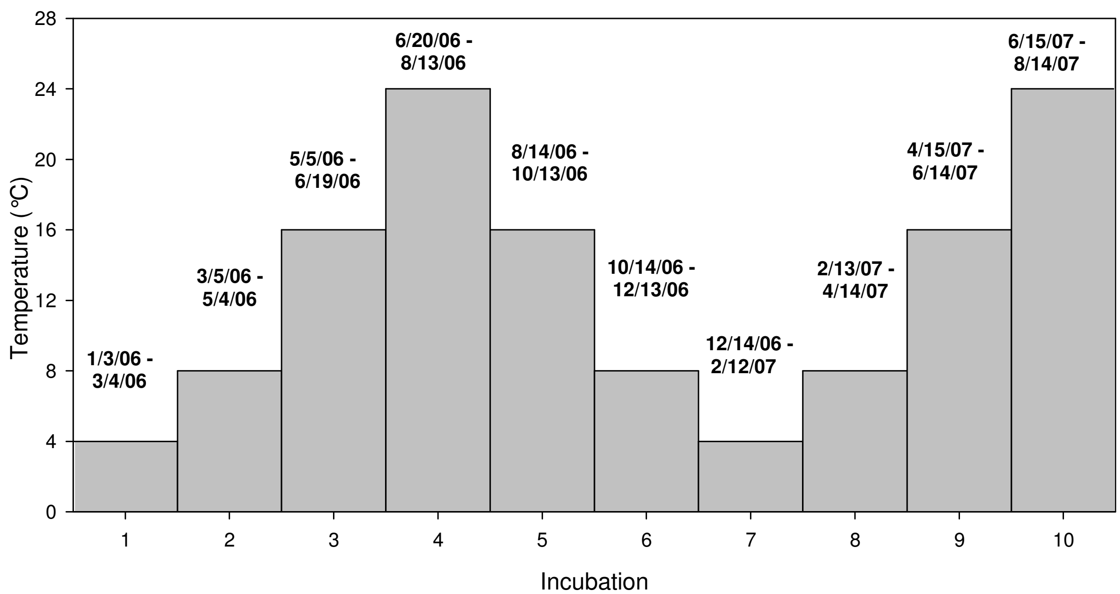

Figure 1. Greenhouse temperature schedule for the current study

In the fall of 2004 all columns, excluding two replicates each of the planted columns, were replanted. For the columns not replanted, one replicate of each plant species was randomly placed into one of two groups of 16 columns. These were used to assess any potential long-term effects on performance. In replanted columns, both gravel and plant material were carefully separated and rinsed of sediment with tap water. Gravel was mixed between replicates within a species, but kept separate by species. Existing sampling ports in the columns allowed redox and water quality measurement at various depths within the column. Because previous research indicated no measurable vertical gradient in water quality (Allen, 1999) and additional concurrent experiments required use of existing redox electrodes, redox and water quality for the current research were measured at a single depth of 15 cm below gravel level. Therefore, existing sampling ports were removed during replanting and replaced with new ports constructed from half-inch (11 mm ID) chlorinated polyvinyl chloride (CPVC) pipe. New pipes were centrally located and inserted to the bottom of the columns. Openings in the CPVC pipe at 15 cm below gravel depth allowed for redox potential measurement. Flexible tygon tubing (0.3 cm ID) was attached to the CPVC pipe for water sample collection at 15 cm depth. Gravel and plant material were then returned to the columns. A water delivery system delivered tap water to the bottom of each column to replace losses due to evapotranspiration and maintain water level just below the gravel surface.

Platinum redox electrodes were constructed according to Faulkner et al. (1989) and placed into sampling ports. A saturated calomel reference electrode was inserted into a salt bridge (Veneman and Pickering, 1983) that connected all columns. Redox measurements were taken every four hours using an analog multiplexer, Labworks II computer interface system (SCI technologies, Bozeman, MT) and personal computer. For reference against the standard hydrogen electrode (SHE) 244 mV were added to redox potential values.

Air and water temperature was measured every 30 minutes using type T thermocouples connected to a Campbell Scientific Inc. (CSI) 21X data logger via AM416 multiplexer and data stored on a SM192 storage module (CSI, Logan, UT). Water temperature was measured ten cm below gravel surface in 16 randomly selected columns. Pore volume in each column was measured periodically throughout the experiment by draining columns completely then filling to just below gravel level using a graduated cylinder.

Establishment and Characterization

During an acclimation and establishment period from January 2005 to November 2005 all 32 columns were operated in 20-day batches using synthetic wastewater simulating secondary domestic effluent (Table 1). Chemical oxygen demand (COD) was analyzed for several 20-day batches during the summer of 2005 in order to characterize columns. In November 2005 the greenhouse temperature was set to 8℃ and columns were randomly placed into two groups. One group of 16 columns operated in alternating 3 and 6-day batches (group A), while the remaining 16 columns were operated in 9-day batches (group B). In January 2006 the 19 month experimental period began.

Operation, Sampling and Analysis

For each 60-day constant temperature incubation, group A columns were operated in six 3-day batches followed by six 6-day batches, or vice versa depending on the previous incubation. If the previous incubation ended with a 6-day batch, then the following incubation began with 6-day batch. The same method was used for 3-day batches. Group B columns were operated in six 9-day batches. To begin each batch, columns were drained for approximately one hour then rapidly refilled with synthetic wastewater recently mixed in a 500-L polypropylene tank. Water quality samples were collected during the last batch of given length within a temperature incubation. During these sampled bacthes influent wastewater was collected for initial concentration values (Table 2) and water samples from columns were collected at day 0 (approximately 30 minutes after filling), days 1, 3, 6, and 9 for appropriate batch lengths. A previous tracer study determined a 5% dilution occurred while filling the wetland columns (Allen, 1999). Therefore, all reported influent concentrations and loading rates are corrected for this dilution factor.

A standard 20 mL Luer-tip syringe was used to collect approximately 12 mL of solution sample (three sampling tube volumes), which was subsequently disposed. A new 20 mL syringe was then used to collect 16 mL of sample and care was taken not to collect any debris or unrepresentative material. Eight mL of sample was placed in a 20 mL glass scintillation vial and then immediately analyzed for COD using colorimetric procedures (0-1500 mg/L Hach Corp., Loveland, CO) and for ammoniacal nitrogen (NH_4-N) using the salicylate method (0-50 mg/L Hach Corp., Loveland, CO). The remaining eight mL of sample was filtered through a 0.2 μm cellulose acetate syringe filter into a glass test tube. The filtered samples were refrigerated at 4°C until analyzed for sulfate, phosphate, and nitrate using ion chromatography (Dionex Co., Sunnyvale, CA). Total nitrogen and nitrite were measured periodically throughout the experimental period using persulfate digestion method (0-25 mg/L Hach Corp., Loveland, CO) and diazotization method (0-0.5 mg/L Hach Corp., Loveland, CO), respectively. Nitrate concentrations were consistently below detection limit (< 1 mg/L) while nitrite levels were < 0.1 mg/L, therefore neither parameter is discussed further. pH was measured periodically using a portable pH meter and was circumneutral (range = 6.86 to 7.34) throughout the experiment.

Statistical Analysis

Water quality for the last batch day is used for the graphical and statistical analysis because effluent values are considered most appropriate for design. Statistical analysis was focused on data from incubation seven (4°C) and incubation ten (24°C) because they were representative of extremes of the overall seasonal performance differences. Analysis of variance (ANOVA) was performed on percent COD and SO_4^{2-} removal and NH_4^+ and PO_4^{3-} concentration ($p = 0.05$) using Minitab Version 15. There were three replicates of planted treatments (those that were not replanted were excluded from the analysis) and four replicates of unplanted controls. ANOVA was also performed on pore volume data for replanted columns (n = six) and columns not replanted (n = 2) for all planted treatments. End-of-batch data (20 days) at identical temperatures within a particular season (four replicates of the same four plant treatments) collected by Allen (1999) are included in the graphical and statistical analysis.

Table 1. Synthetic wastewater composition

Reagent	**Concentration (mg/L)**
$C_{12}H_{22}O_{11}$	200
Primatone	222
$FeCl_3$	0.4
$MgSO_47H_20$	62
K_2HPO_4	44
NH_4Cl	57.4
H_3BO_3	10
$CuSO_4$	0.8
KI	1.9
$MnSO_4$	7.8
Na_2MoO_4	4.0
$ZnSO_4$	7.8
$CaCl_2$	1.9

Table 2. Mean influent wastewater parameters (mg/L) ± one standard deviation

BOD_5*	COD	NH_4-N	TN	PO_4-P	SO_4-S	pH
283	**436 ± 26**	**14.9 ± 1.4**	**41 ± 4.3**	**6.9 ± 1.2**	**13.5 ± 2.5**	**7.1 ± 0.1**

*BOD_5 was only measured once. The reported value is determined by multiplying the BOD_5:COD ratio (0.65) and mean COD for all measurements.

RESULTS AND DISCUSSION

Pore Volume Measurements

Pore volume for all treatments was measured periodically over 24 months (Figures 2 and 3). Porosity differences between columns replanted in 2004 and columns planted in 1997 (not replanted) were statistically significant on all measurement dates and for all species except for *Typha* in the fall of 2006 and summer of 2007 and *Schoenoplectus* in summer of 2007. Pore volume for *Carex* and *Schoenoplectus* was approximately one-fifth lower in columns not replanted than in replanted columns and about one-seventh lower in *Typha* columns. A seasonal pattern in porosity is apparent in planted treatments where winter porosities are generally lower than summer porosities. Though the magnitude varies somewhat the pattern is strikingly consistent across all plant species and time since planting. Though this pattern is counter-intuitive it is presumably a result of growth and senescence of below ground plant material. However, pore volume was measured to the gravel surface level, which was assumed constant, but not checked during each measurement date. Therefore, a seasonal increase in the amount of root mass could have decreased the interstitial porosity but could also have expanded the entire gravel depth or both. The approxiamate magnitude of the seasonal change could be due to a change in gravel depth of 2-4 cm. It is not known whether seasonal changes in root mass influenced the interstitial pore volume or simply changed gravel levelRegardless, a larger pore

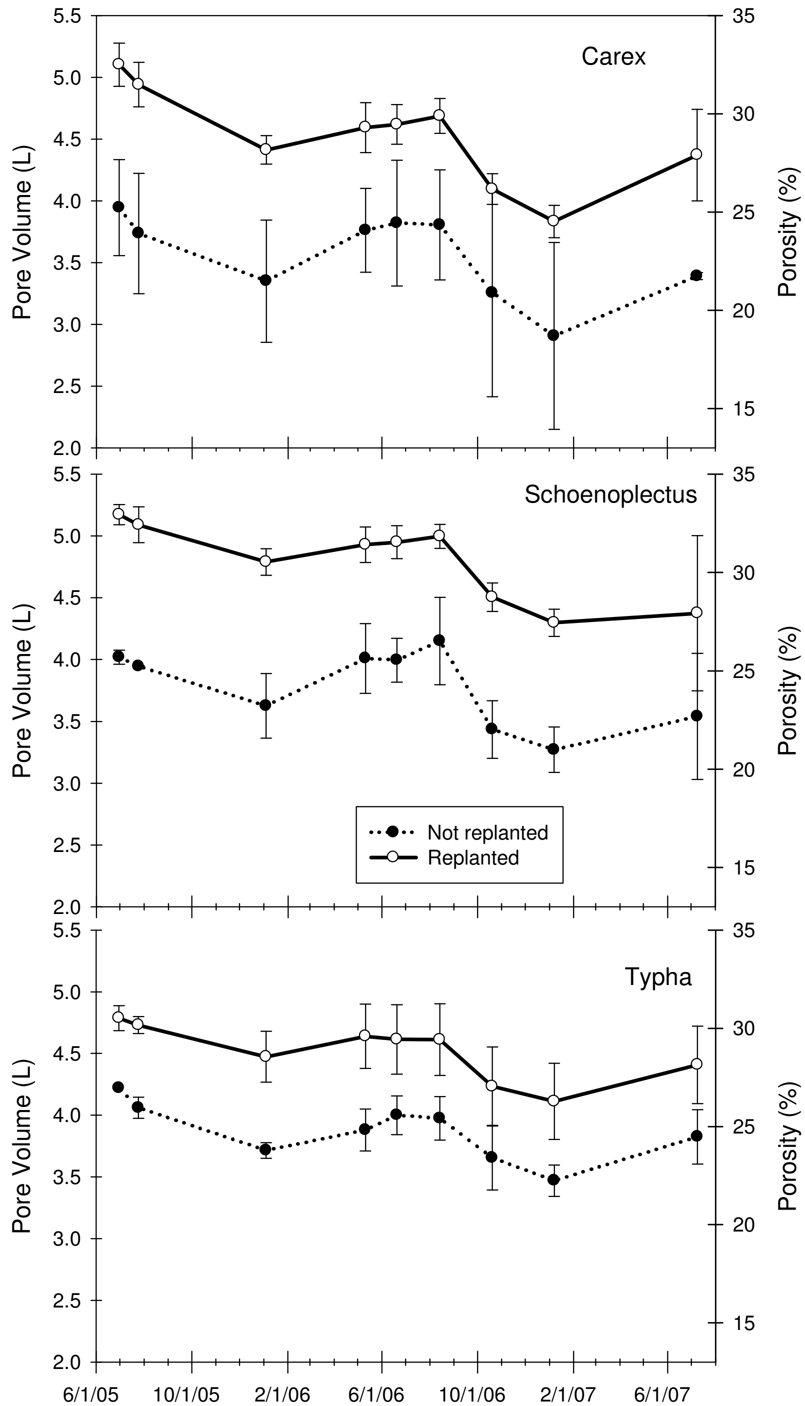

Figure 2. Pore volume for replanted and not replanted columns (means ± one standard deviation). n = 2 for columns not replanted and n = 6 for replanted columns.

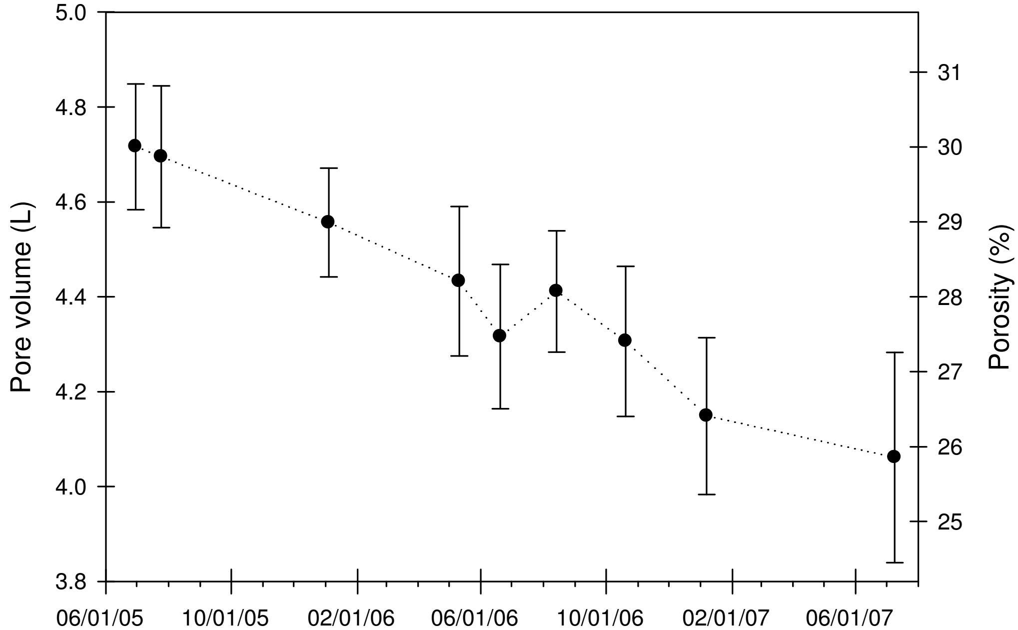

Figure 3. Pore volume for unplanted controls (mean of eight replicates ± one standard deviation).

volume in summer indicates a larger treatment volume per unit area and increases the mass loading rate for a constant influent pollutant concentration.

Measurement of pore volume in unplanted controls showed no seasonal changes (Figure 3). However, as with planted treatments there was an overall decrease in measured pore volume with time. Over 24 months there was a 0.7 L and 4% decrease in pore volume and porosity (pore volume/ total volume), respectively for unplanted controls. By comparison, an average decrease of 0.6 L in pore volume (3% porosity) was seen in planted treatments. The suspended solids concentration for the synthetic wastewater used was negligible, so accumulation of influent solids would not contribute significantly to a decrease in void space. Root and biofilm growth and/or settling of gravel could lead to decreased porosity in the columns. However, a decrease in gravel depth of approximately 7-8 cm would be required solely explain this decrease in pore volume. While seasonal variation of 2-4 cm in planted columns may have gone unnoticed, unplanted column depth did not decrease by this amount, suggesting biofilm growth is a significant contributor to the decreased porosity. A decrease in porosity was noted in a similar study and also attributed to root and rhizome growth in planted treatments and biofilm growth in unplanted treatments (Tanner et al. 1999).

Because pore volume was significantly lower in columns that were not replanted, the loading rate was also lower for these columns. An effort was made to normalize all planted columns to this effect, but no practical value could be determined. Therefore, only replanted columns are used in the data analysis that follows, resulting in three replicates of each plant species in each group and four replicates of unplanted controls in each group.

Seasonal Patterns in Water Quality and Redox Potential

End of batch data for percent COD and SO_4^{2-} removal, redox potential, and NH_4^+ and PO_4^{3-} concentration over the entire study period and for 32 kg/ha•d collected at virtually identical conditions by Allen (1999) are presented in figures 4–8. Differences in seasonal trends for COD removal are apparent between plant treatments and generally speaking, COD removal in planted treatments was higher at lighter loading rates (32 and 70 kg COD/ha•d). The lighter loadings also tended to have greater seasonal variation differences between treatments, especially during the second half of the study. Relative to other treatments, COD removal in *Carex* was lower during summer incubations and higher during winter incubations at the two higher loading rates (Figure 4). Unplanted controls showed a more pronounced seasonal COD removal effect with better performance at warmer temperatures and also displayed a comparative insensitivity to loading rate. Even with a yearlong acclimation period all treatments showed a start-up effect where COD removal is generally lower for earlier incubations compared to later incubations with equivalent temperatures.

SO_4^{2-} removal at lighter loading rates (32 and 70 kg COD/ha•d) was influenced by treatment and temperature (Figure 5). For *Carex* and *Schoenoplectus,* SO_4^{2-} removal was virtually complete at warmer temperatures but decreased during cooler temperatures. However, a start-up effect can again be noted where this decrease in SO_4^{2-} removal was not evident in earlier incubations. There was also a decrease in SO_4^{2-} removal for 105 kg COD/ha•d at 4°C, but was it was less than for the lower loading rates. SO_4^{2-} removal for the highest loading rate was essentially constant through out the experimental period, remaining around 90-100% removal for all treatments. *Typha* and control treatments removed 90-100% of the influent sulfate at all loading rates and temperatures.

The redox potential data tends to support the seasonal pattern of root zone oxidation status suggested by the SO_4^{2-} data (Figure 6). While occasional scatter is apparent, redox potential is almost always below -100 mV throughout the study period for all treatments at 105 and 210 kg COD/ha•d and for *Typha* and control for all loading rates. However redox potential at cooler temperatures increases somewhat at 70 kg/ha•d and greatly at 32 kg/ha•d in *Carex* and *Schoenoplectus* columns. These periods of increased redox coincide with periods of less sulfate removal and less temperature sensitivity in COD removal. The increased redox potential for the highest loaded planted treatments at 24°C might reflect higher evapotranspiration rates which either lowered the water level by exceeding the water delivery rate and/or increasing the supply of oxygenated replacement water.

Planted treatments showed some seasonality in ammonium concentration with lower concentrations during warmer incubations (Figure 7) for all loading rates. Ammonium concentrations in *Carex* columns were lower than all other treatments for all loading rates. Unplanted controls consistently have the largest NH_4^+ concentration, up to 30 mgN/L and showed an overall increase in NH_4^+ concentration throughout the experiment, suggesting plants significantly increase the removal of NH_4^+ and alter seasonal pattern. The synthetic wastewater used contained approximately 26 mg/L organic nitrogen and approximately 15 mg/L ammonium N. The conversion of organic nitrogen to NH_4^+ could explain NH_4^+ concentrations greater than influent concentrations as is most evident in unplanted controls. All planted treatments performed similarly at the two lowest loading rates, but as loading rate was increased, *Typha* and *Schoenoplectus*

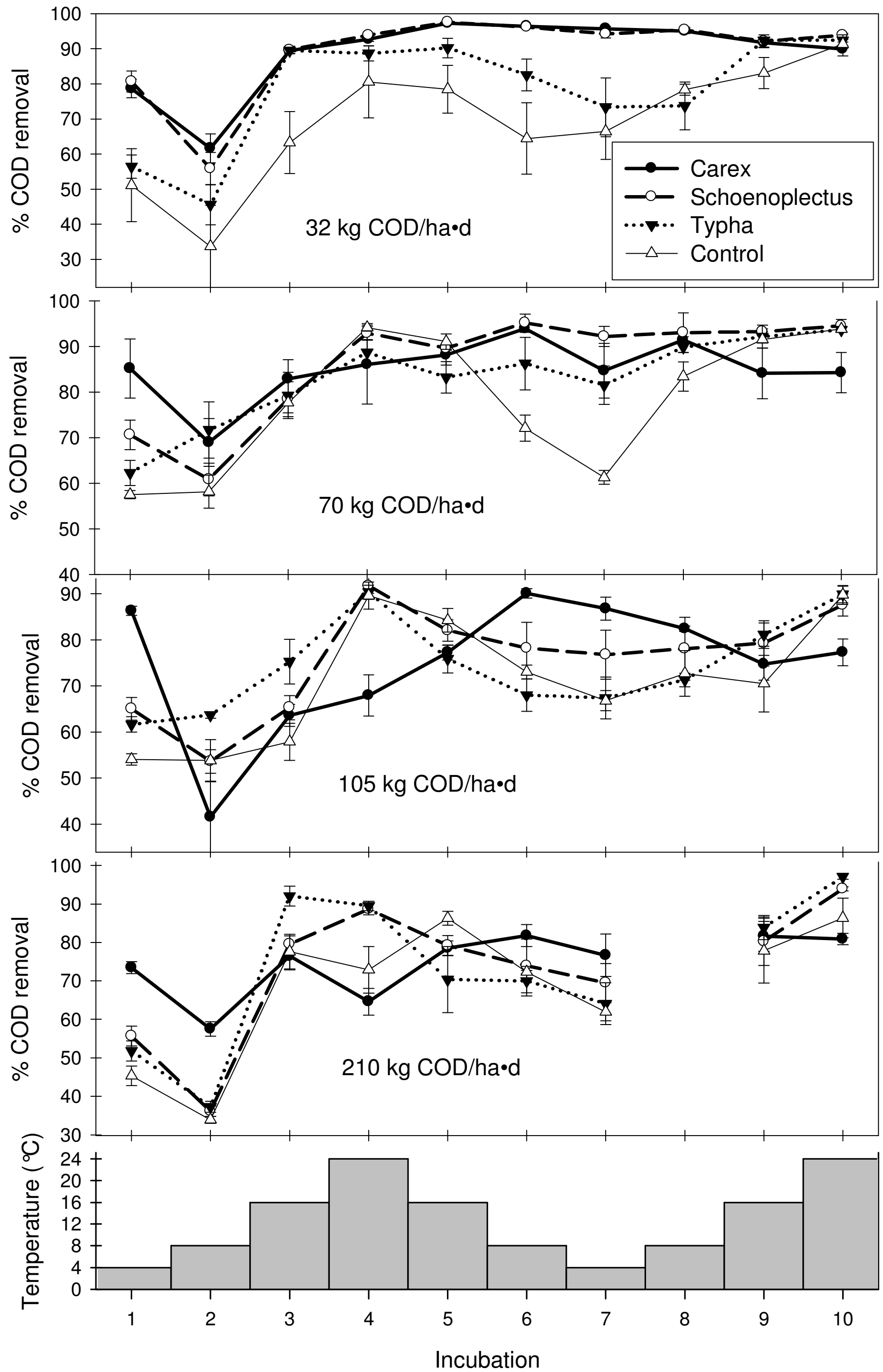

Figure 4. Seasonal patterns of COD removal. Values are mean removal on last batch day ± one standard error. Loading rates 32, 70, 105, and 210 kg COD/ha•d correspond to 20, 9, 6, and 3 day batch lengths, respectively. 32 kg COD/ha•d data collected by Allen (1999).

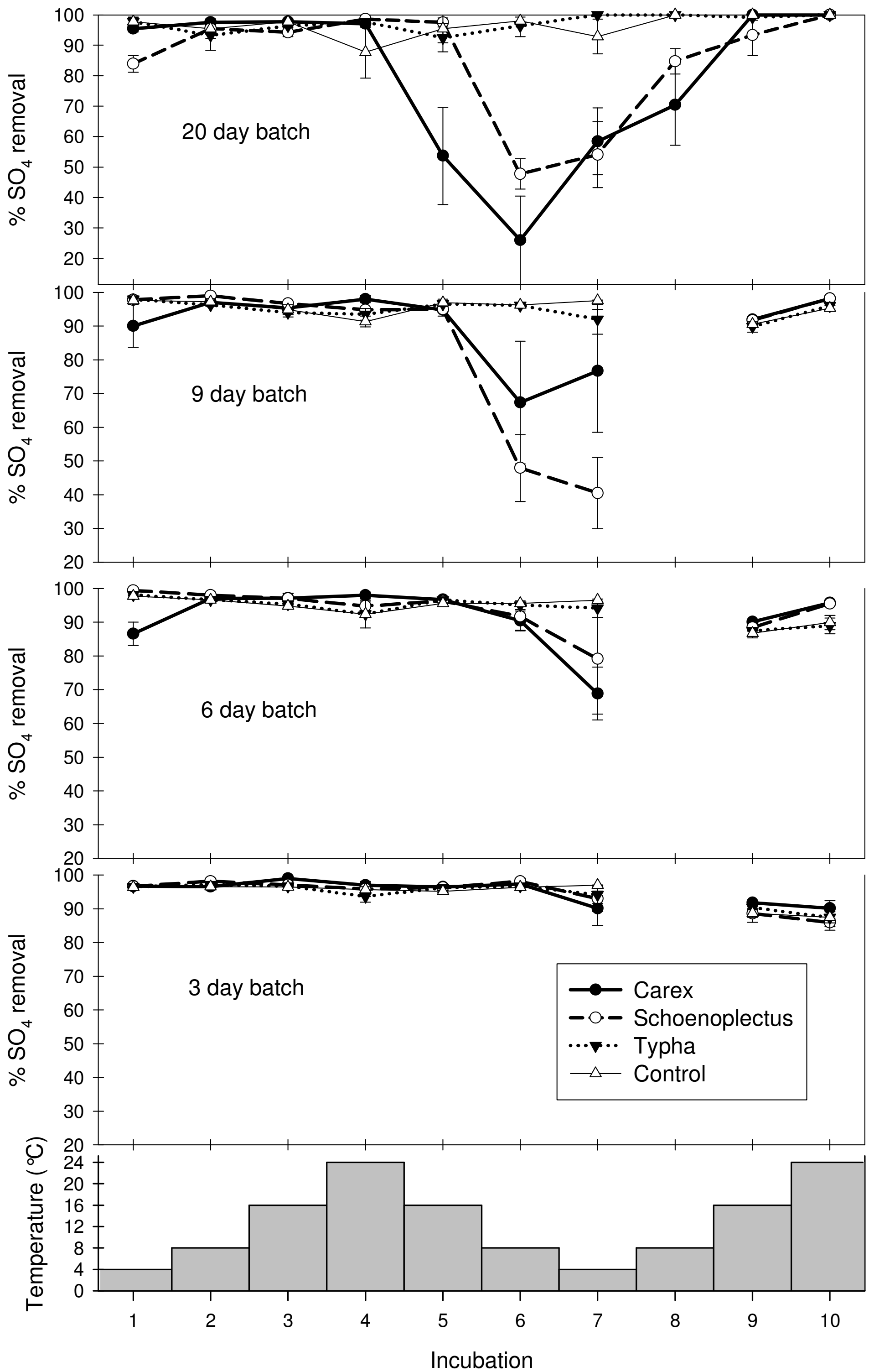

Figure 5. Seasonal patterns of SO_4^{2-} removal. Values are mean removal on last batch day ± one standard error. 20 day data collected by Allen (1999).

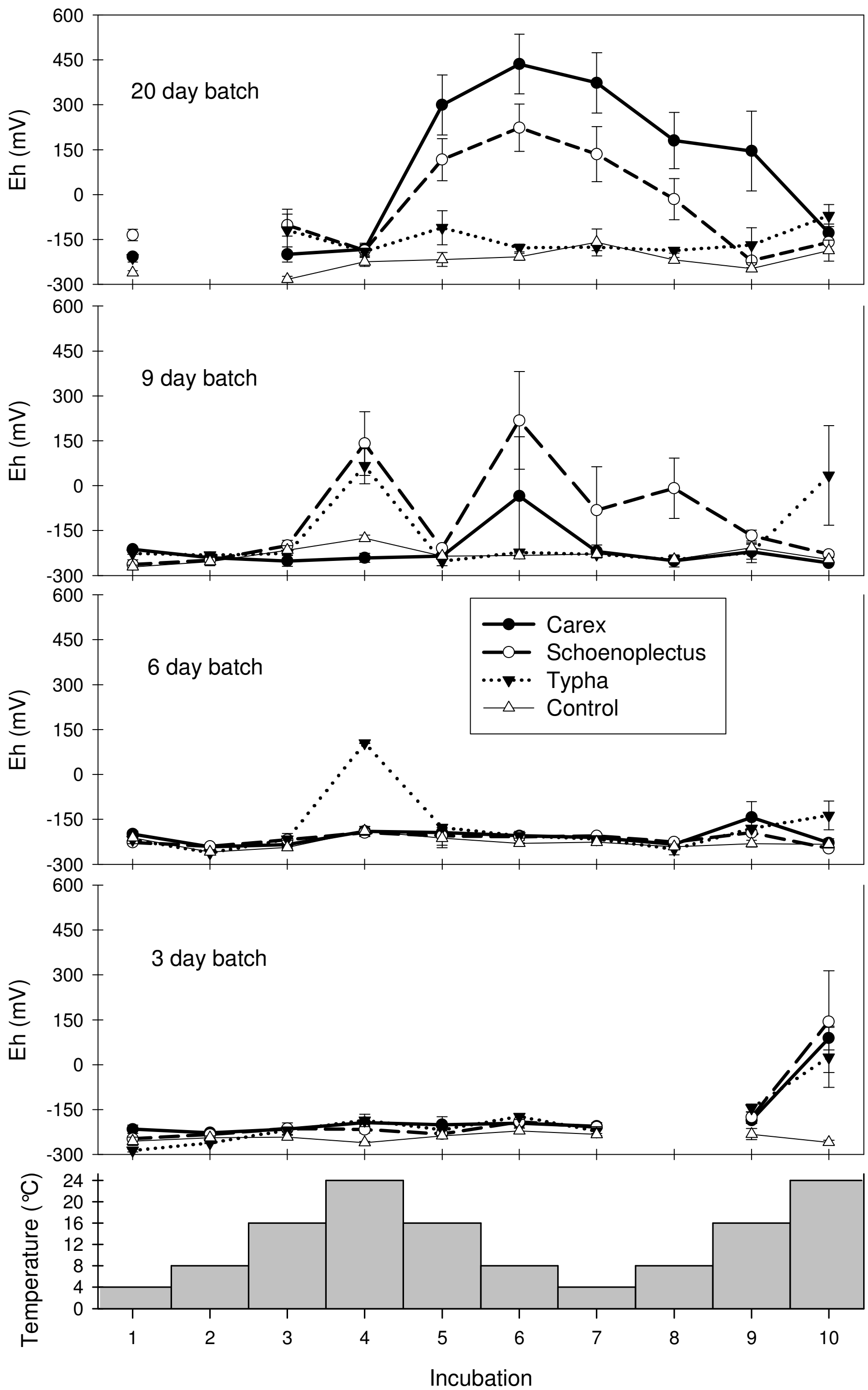

Figure 6. Seasonal patterns of redox potential. Values are mean removal on last batch day ± one standard error. 20 day data collected by Allen (1999).

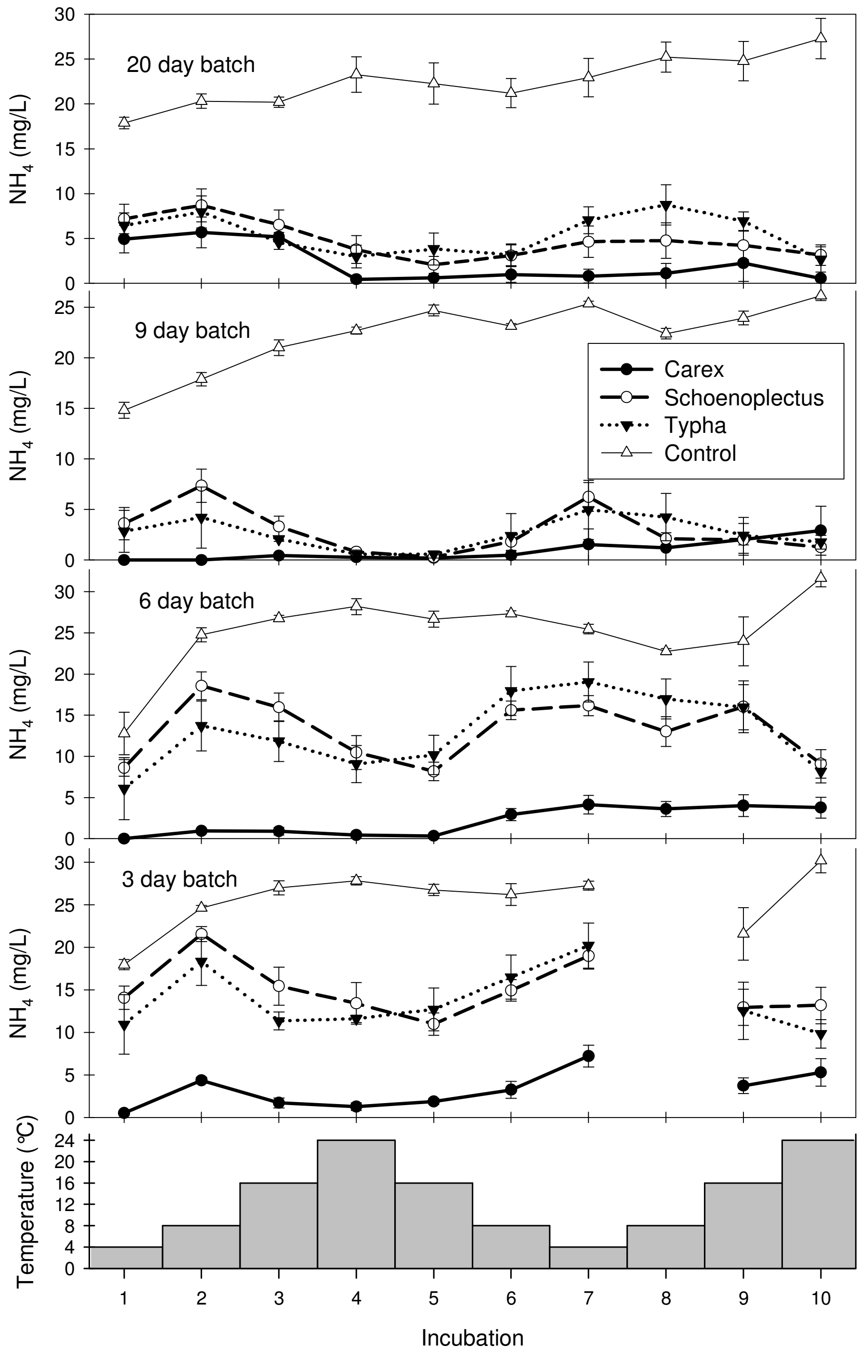

Figure 7. Seasonal patterns of NH_4^+ concentration. Values are mean concentration on day three ± one standard error. Average influent concentration were 41.3 for TN and 15 for NH_4^+. 20 day data collected by Allen (1999).

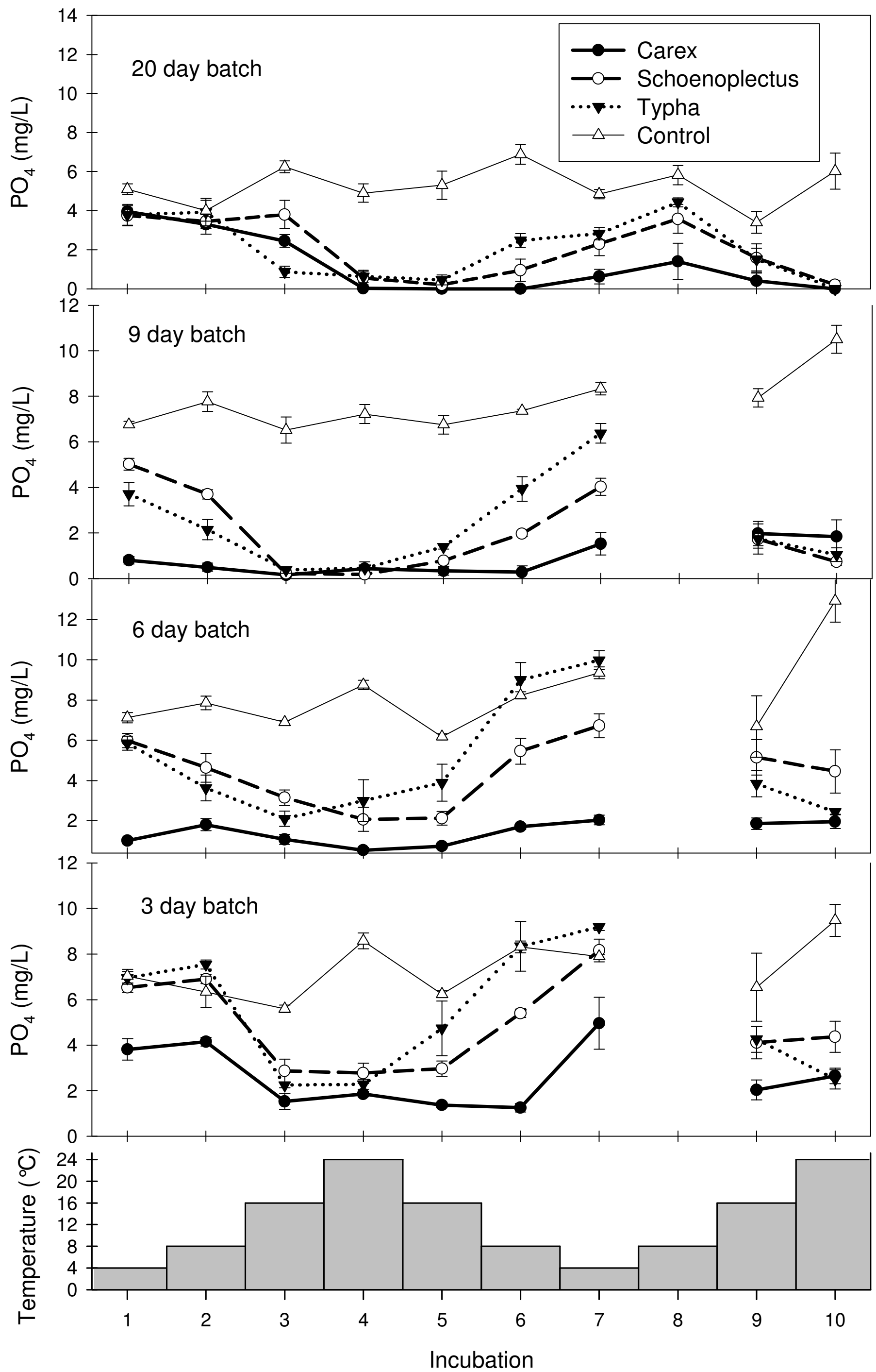

Figure 8. Seasonal patterns of PO_4^{3-} removal. Values are mean removal on day three ± one standard error. 20 day data collected by Allen (1999).

columns performed similarly and not as well as *Carex*.

For most incubations phosphate concentration was lowest in *Carex* columns at all loading rates (Figure 8). Planted treatments showed some seasonality in PO_4^{3-} concentration with lower concentrations during warmer incubations. PO_4^{3-} concentration in unplanted controls was approximately equal to influent PO_4^{3-} concentration during the experiment. PO_4^{3-} concentrations were higher at higher loading rates for planted treatments. Evidence for sorption as a removal mechanism is mixed as PO_4^{3-} concentration did not increase greatly with time but did with loading rate. Concentrations of PO_4^{3-} greater than influent concentrations are difficult to explain. Possible explanations are formation of PO_4^{3-} and desorption, though as noted above sorption may not be an important removal mechanism.

Water Quality at 24°C and 4°C

COD removal for incubations seven (4°C) and ten (24°C) are presented in Figure 9 and Tables 3 and 4. COD removal is typically higher at 24°C for most treatments, especially at higher loading rates, with the exception of *Carex* which usually had decreased performance at 24°C. The influence of loading rate was most prevalent for *Carex* and *Schoenoplectus* at 4°C where COD removal decreased with increasing loading rate. An inverse relationship between COD removal and loading rate has been found by other researchers as well (Tanner et al., 1995; Akratos and Tsihrintzis, 2007). COD removal was poor at 4°C for

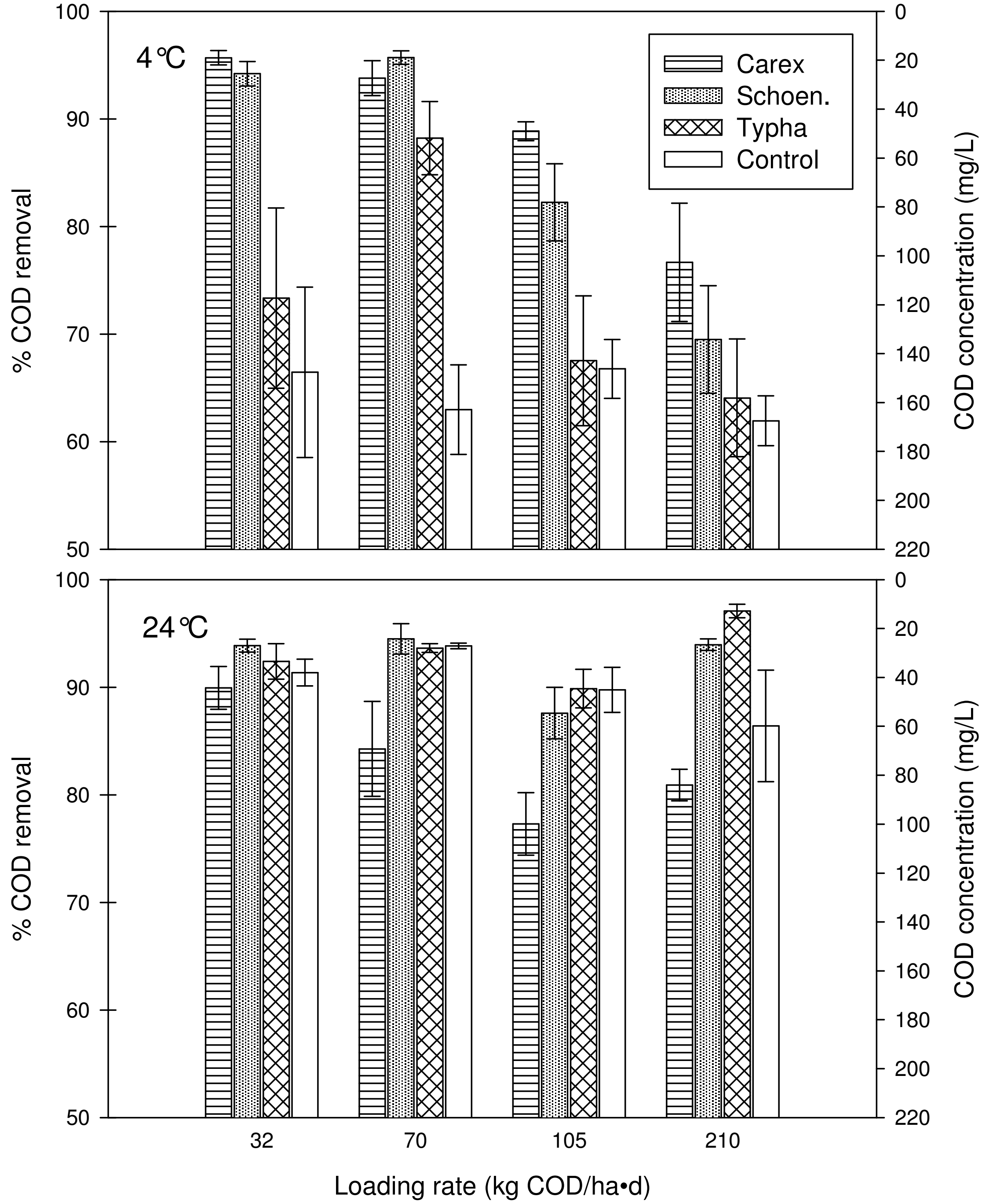

Figure 9. COD removal at incubation seven (4°C) and incubation ten (24°C) (means ± one standard error). Values are for last batch day for each batch length. Loading rates 32, 70, 105, and 210 kg COD/ha•d correspond to 20, 9, 6, and 3 day batch lengths, respectively.

Table 3. Influence of loading rate on COD removal

	4℃				24℃			
kg COD/ha•d	**Carex**	**Sch.**	**Typha**	**Control**	**Carex**	**Sch.**	**Typha**	**Control**
32	95.7 B	94.2 BC	73.4 A	66.5 A	89.9 AC	93.9 A	92.4 AB	91.4 A
70	93.8 B	95.7 C	88.2 A	63.0 A	84.3 A	94.5 A	93.6 AB	93.8 A
105	88.9 AB	82.2 AB	67.5 A	66.8 A	77.3 AB	87.6 B	89.9 B	89.7 A
210	76.7 A	69.5 A	64.1 A	61.9 A	80.9 A	94.0 A	97.1 A	86.4 A

Values are mean percent COD removal on last batch day. For each temperature matching letters within a column represent loading rates that are not significantly different within species.

Table 4. Influence of species on COD removal

	4℃ (kg COD/ha•d)				24℃ (kg COD/ha•d)			
Species	**32**	**70**	**105**	**210**	**32**	**70**	**105**	**210**
Carex	95.7 A	93.8 A	88.9 A	76.7 A	89.9 A	84.3 A	77.3 A	80.9 A
Schoen.	94.2 A	95.7 A	82.2 AB	69.5 A	93.9 A	94.5 B	87.6 AB	94.0 AB
Typha	73.4 AB	88.2 A	67.5 B	64.1 A	92.4 A	93.6 AB	89.9 B	97.1 B
Control	66.5 B	63.0 B	66.8 B	61.9 A	91.4 A	93.8 B	89.7 B	86.4 AB

Values are mean percent COD removal on last batch day. For each temperature matching letters within a column represent plant species that are not significantly different within a loading rate.

Typha and unplanted controls and there was no significant difference between loading rates at either temperature. COD removal for all loading rates in

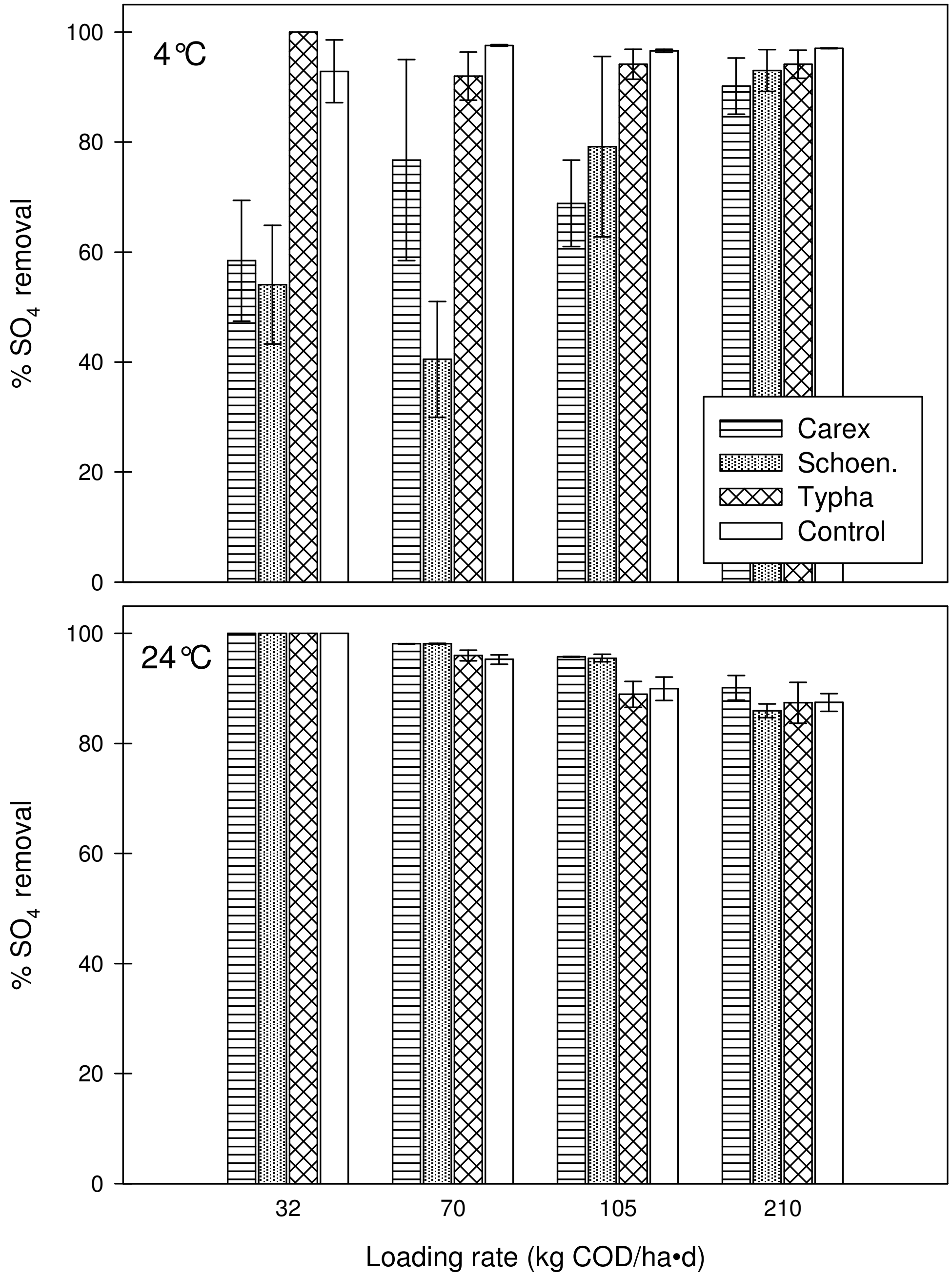

Figure 10. SO_4^{2-} removal at incubation seven (4°C) and incubation ten (24°C) (means ± one standard error). Values are for last batch day for each batch length. Loading rates 32, 70, 105, and 210 kg COD/ha•d correspond to 20, 9, 6, and 3 day batch lengths, respectively.

Table 5. Influence of species on SO_4^{2-} removal

	4°C (kg COD/ha•d)				24°C (kg COD/ha•d)			
Species	**32**	**70**	**105**	**210**	**32**	**70**	**105**	**210**
Carex	58.4 $_A$	76.7 $_A$	68.8 $_A$	90.2 $_A$	100 $_A$	98.1 $_A$	97.8 $_A$	90.1 $_A$
Schoen.	54.1 $_A$	40.5 $_{AB}$	79.2 $_A$	93.0 $_A$	100 $_A$	98.2 $_A$	95.5 $_A$	86.0 $_A$
Typha	100 $_B$	92.0 $_A$	94.2 $_A$	94.1 $_A$	100 $_A$	96.0 $_A$	89.0 $_A$	87.4 $_A$
Control	92.9 $_B$	97.6 $_A$	96.6 $_A$	97.0 $_A$	100 $_A$	95.3 $_A$	90.0 $_A$	87.5 $_A$

Values are mean percent SO_4^{2-} removal on last batch day. For each temperature matching letters within a column represent plant species that are not significantly different within loading rates.

unplanted controls was not significantly different at 24°C, while performance varied for planted treatments.

Generally speaking plants tended to improve winter wetland performance at 4°C by increasing COD removal, especially in *Carex* and *Schoenoplectus* columns at lighter loading rates. However, as loading rate increased treatment effects diminished and there were no significant differences between any of the treatments at the highest loading rate. The ability of *Carex*, and to a lesser degree *Schoenoplectus*, to negate temperature effects for COD removal found by Allen et al. (2002) and Hook et al. (2003) is supported here, but it appears that root zone oxidation status is reduced by increasing the COD loading rate. Sulfate and redox potential data at 24°C and 4°C (Figures 10 and 11, Table 5) strongly suggest an anaerobic environment supporting sulfate reducing bacteria (SRB) activity is prevalent for most treatments as there are no

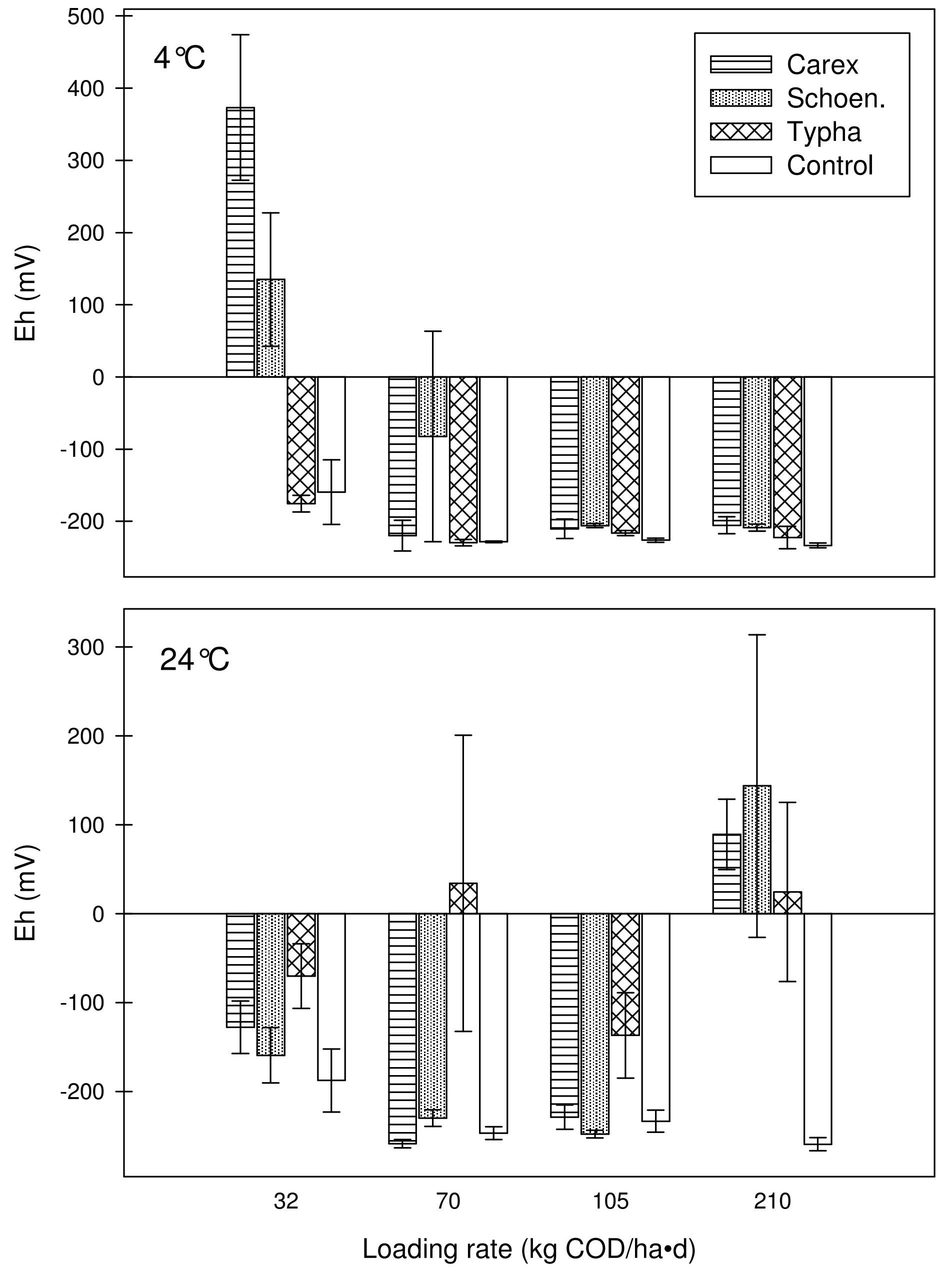

Figure 11. Redox potential at incubation seven (4°C) and incubation ten (24°C) (means ± one standard error). Values are for last batch day for each batch length. Loading rates 32, 70, 105, and 210 kg COD/ha•d correspond to 20, 9, 6, and 3 day batch lengths, respectively.

differences in sulfate removal between species or loading rates at 24°C. However, *Carex* and *Schoenoplectus* at 4°C show decreased SO_4^{2-} removal and increased redox potential at the lower loading rates, consistent with better COD removal compared to other conditions. Sulfate removal for *Carex* and *Schoenoplectus* is significantly worse than *Typha* and control at 32 kg COD/ha•d but sulfate removal increases with increased loading and no species differences are apparent by 105 kg COD/ha•d. Redox data display more scatter, but are consistent with sulfate data in that highly reduced conditions supporting anaerobic breakdown of COD are apparent for all treatments at 24°C, *Typha* and control at all temperatures, and *Carex* and *Schoenoplectus* at higher loading rates.

Ammonium concentration data at 24°C and 4°C are shown in figure 12. Though influent ammonium averaged only 15 mg/L there was an additional 26 mg/L organic N. A comparison between NH_4^+ and total nitrogen (TN) after 24 hours (Figure 13) shows that most organic N was rapidly hydrolyzed to NH_4^+, consistent with results of (Allen 1999). Therefore, NH_4^+ concentration data are assumed approximately equal to TN concentration after one day. Plants increased NH_4^+ removal for most loading rates at 4°C and especially at 24°C (Table 6). Differences between planted treatments at 4°C are not significant at 32 and 70 kg COD/ha•d, but as loading rate is increased *Carex* has a significantly lower NH_4^+ concentration than all other treatments (Table 6). At

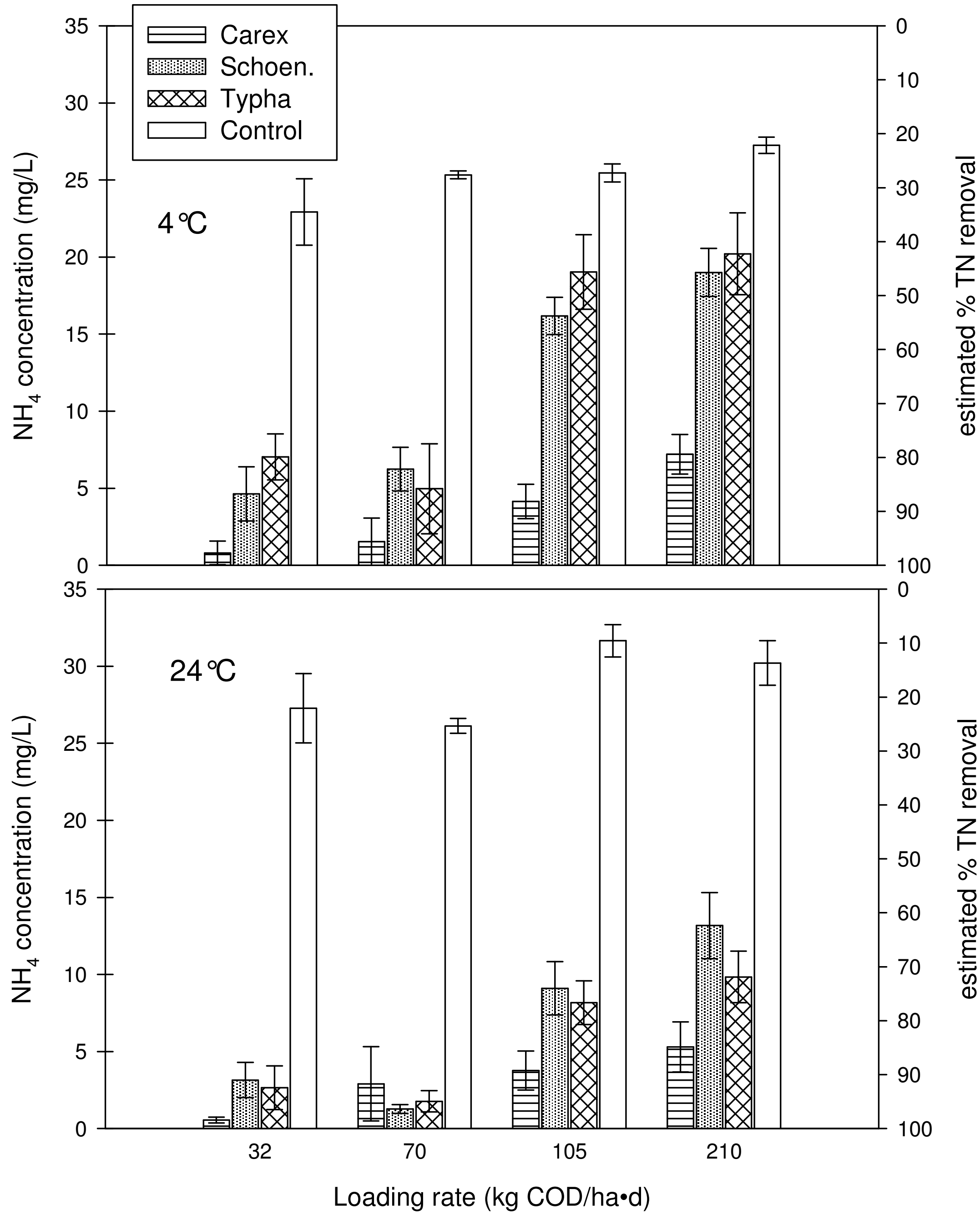

Figure 12. NH_4^+ at incubation seven (4℃) and incubation ten (24℃) (means ± one standard error). Loading rates 32, 70, 105, and 210 kg COD/ha•d correspond to 20, 9, 6, and 3 day batch lengths, respectively. TN removal estimated from input TN and the assumption that all organic N is converted to NH_4^+ by the end of the batch.

.

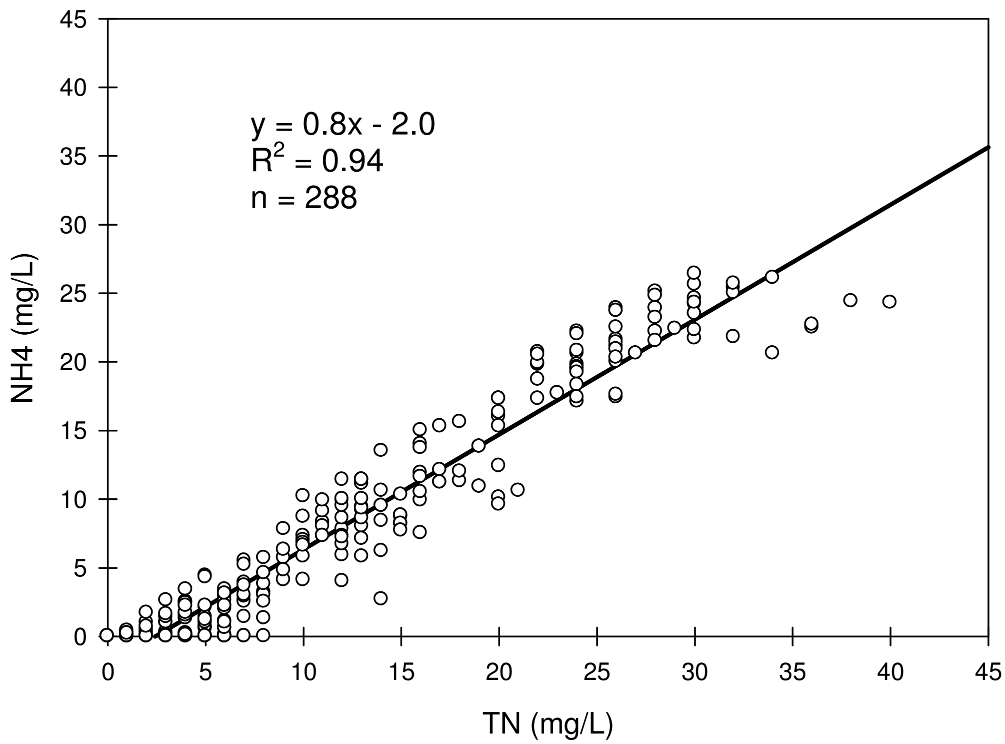

Figure 13. Linear regression of total nitrogen (TN) against ammonium (NH_4^+). Data includes days one to nine.

Table 6. Influence of species on NH_4^+ concentration

	4°C (kg COD/ha•d)				**24°C (kg COD/ha•d)**			
Species	**32**	**70**	**105**	**210**	**32**	**70**	**105**	**210**
Carex	0.8 $_A$	1.5 $_A$	4.1 $_A$	7.2 $_A$	0.6 $_A$	2.9 $_A$	3.8 $_A$	5.3 $_A$
Schoen.	4.6 $_A$	6.2 $_A$	16.2 $_B$	19.0 $_B$	3.2 $_A$	1.3 $_A$	9.1 $_A$	13.2 $_B$
Typha	7.0 $_A$	5.0 $_A$	19.0 $_B$	20.2 $_B$	2.7 $_A$	1.8 $_A$	8.2 $_A$	9.8 $_{AB}$
Control	22.9 $_B$	25.3 $_B$	25.5 $_C$	27.3 $_C$	27.3 $_B$	26.1 $_B$	31.7 $_B$	30.2 $_C$

Values are mean NH_4^+ concentration on last batch day. For each temperature matching letters within a column represent plant species that are not significantly different within loading rates.

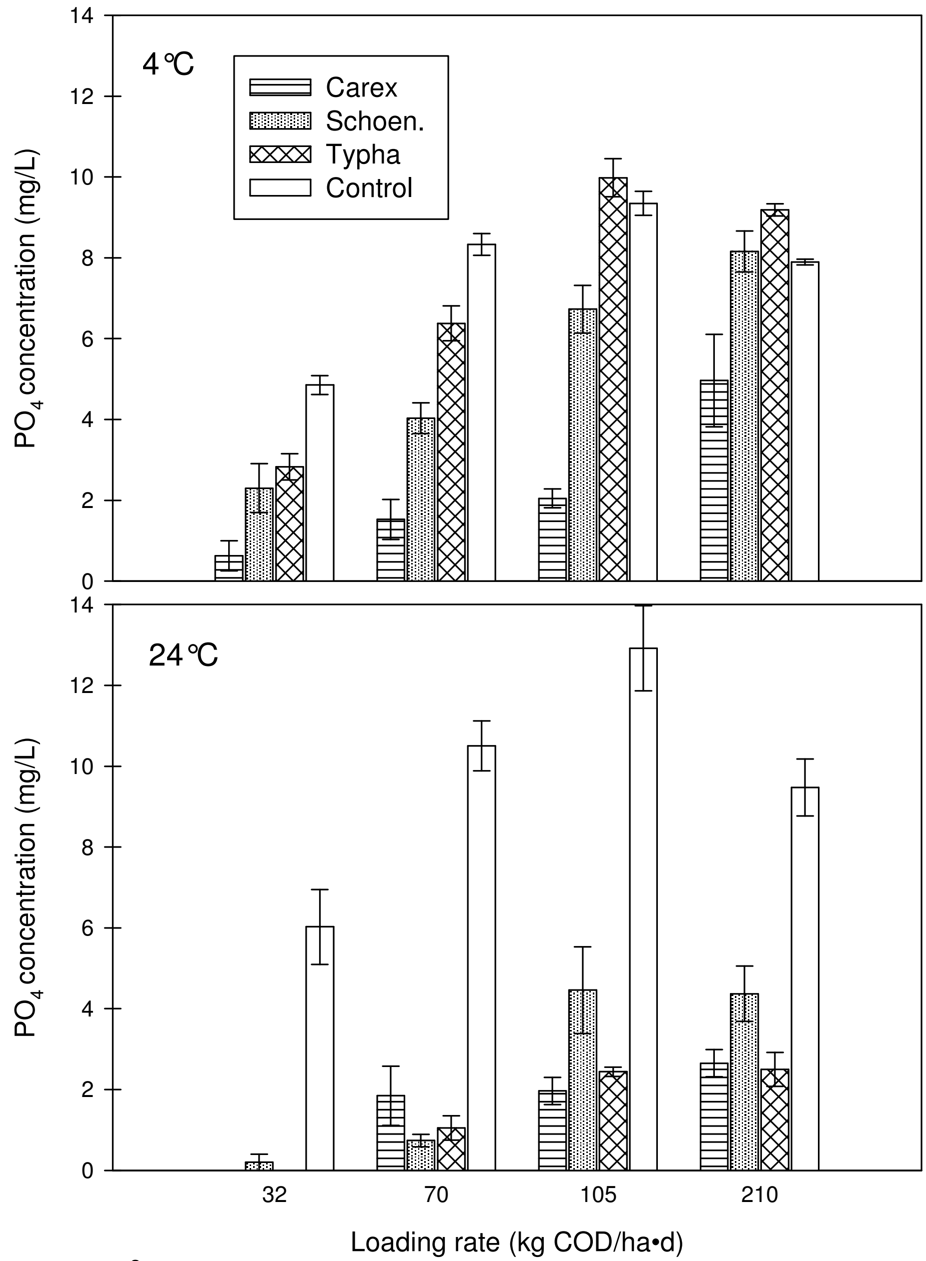

Figure 14. PO_4^{3-} at incubation seven (4°C) and incubation ten (24°C) (means ± one standard error). Values are for last batch day for each batch length. Loading rates 32, 70, 105, and 210 kg COD/ha•d correspond to 20, 9, 6, and 3 day batch lengths, respectively.

Table 7. Influence of species on PO_4^{3-} concentration

	4°C (kg COD/ha•d)				24°C (kg COD/ha•d)			
Species	**32**	**70**	**105**	**210**	**32**	**70**	**105**	**210**
Carex	0.6 $_A$	1.5 $_A$	2.1 $_A$	5.0 $_A$	0 $_A$	1.9 $_A$	2.0 $_A$	2.7 $_A$
Schoen.	2.3 $_{AB}$	4.0 $_B$	6.7 $_B$	8.2 $_B$	0.2 $_A$	0.7 $_A$	4.5 $_A$	4.4 $_A$
Typha	2.8 $_B$	6.4 $_C$	10.0 $_C$	9.2 $_B$	0 $_A$	1.1 $_A$	2.4 $_A$	2.5 $_A$
Control	4.9 $_C$	8.3 $_D$	9.4 $_C$	7.9 $_B$	6.0 $_B$	10.5 $_B$	12.9 $_B$	9.5 $_B$

Values are mean PO_4^{3-} concentration on last batch day. For each temperature matching letters within a column represent plant species that are not significantly different within loading rates.

24°C differences between planted treatments are not significant except at the highest loading rate.

Phosphate concentration data at 24°C and 4°C are shown in figure 13. At 24°C PO_4^{3-} concentrations for planted treatments were significantly lower than unplanted controls for all loading rates. There was no difference between plant species at 24°C at any loading rate. At 4°C PO_4^{3-} concentrations in *Carex* were significantly lower than all other treatments and as loading rate decreased performance varied (Table 5).

Plant uptake and/or adsorption are two mechanisms by which N and P can be removed. Plant roots provide an increased sorption surface area and as discussed previously may increase redox potential during winter at lighter loading rates. Sequential nitrification-denitrification which is suggested by the data may be enhanced by more available oxygen. If plant uptake were a significant removal mechanism then at the two higher loadings rates *Carex* would be 2-3 times larger than *Schoenoplectus* and *Typha*. Therefore, evidence is strong for sequential nitrification-denitrification and/or sorption followed by utilization. Determining the removal mechanism(s) would require additional, more detailed, experiments.

CONCLUSIONS

Under the conditions of this experiment planted treatments generally improved performance of the model wetland system by increasing COD, NH_4^+, and PO_4^{3-} removal. The positive influence of species was more apparent during the winter season than during the growing season. However as loading rate was increased the improved performance of *Carex* and *Schoenoplectus* at 4°C was diminished. At higher loadings, removal of wastewater constituents in planted treatments was better at 24°C which would be expected for microbially mediated pollutant transformation.

The range of temperature and loading rate used in this study brackets most practical applications and results are generally consistent with similar research within narrower ranges. Before loading rate, or batch lengths, could be recommended for design, however, it would be advised to carry out experiments in the field under conditions similar to potential operating conditions. The data presented here suggests loading rates of 105 kg COD/ha•d and higher may inhibit any benefit provided by some plant species such as *C. utriculata* and *S. acutus* due to increased rhizosphere oxygenation during the winter season. Results should be interpreted with caution. Although relative performance of treatments could be expected in practical applications (field-scale wetlands, domestic wastewater, etc.), actual performance may vary. Loading rate was changed by varying batch length in this study, but could also be changed by changing wetland size or wastewater pollutant concentration. Results could be different than noted here if loading rate was varied by changing other parameters.

Further studies into the seasonal porosity change noted here could improve knowledge about possible changes in wetland hydrology hitherto not considered. Although not the focus of the current research, changes in wetland pore volume would have tremendous impact on the design and long-term performance of constructed wetlands.

REFERENCES

Akratos, C.S., Tsihrintzis, V.A. (2007). Effect of temperature, HRT, vegetation and porous media on removal efficiency of pilot-scale horizontal subsurface flow constructed wetlands. Ecol. Eng. *29*(2), 173-191.

Allen, W.C. (1999). Seasonal plant effects on wastewater treatment and root-zone oxidation in model wetlands. M.S. Thesis. Montana State University, Bozeman, MT.

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.

Behrends, L., Houke, L., Bailey, E., Jansen, P., Brown, D. (2001). Reciprocating constructed wetlands for treating industrial, municipal, and agricultural wastewater. Wat. Sci. Tech., *44*(11-12), 399-406.

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

Brix, H. (1994). Use of Constructed Wetlands in Water Pollution Control: Historical Development, Present Status, and Future Perspectives. Water Sci. and Technol. *30*, 209-223.

Burgoon, P.S., Reddy, K.R., Debusk, T.A. (1995). Performance of Subsurface Flow Wetlands with Batch-Load and Continuous-Flow Conditions. Wat. Environ. Res. *67* (5), 855-862.

Busnardo, M.J., Gersberg, R.M., Langis, R., Sinicrope, T.L., Zedler, J.B. (1992). Nitrogen and phosphorus removal by wetland mesocosms subjected to different hydroperiods. Ecol. Eng. *1*(4), 287-307.

Faulkner, S.P., Patrick, Jr., W.H., Gambrell, R.P. (1989). Field techniques for measuring wetland soil parameters. Soil Sci. Am. J. *53*, 883-890.

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.

Jing, S.R., Lin, Y.F., Wang, T.W., Lee, D.Y. (2002). Microcosm Wetlands for Wastewater Treatment with Different Hydraulic Loading Rates and Macrophytes. J. Environ. Qual. *31*(2), 690-696.

Kadlec, R.H., Knight, R.L. (1996). Treatment Wetlands. CRC Press, Boca Raton, Florida, United States

Mitsch, W.J., Gosselink, J.G. (1993). Wetlands (2nd ed.). Van Nostrand Reinhold Company, New York, United States.

Stein, O.R., Hook, P.B., Bierderman, J.A., Allen, W.C., Borden, D.J. (2003). Does batch operation enhance oxidation in subsurface constructed wetlands? Wat. Sci. Tech. *48*(5), 149-156.

Sun, G., Zhao, Y., Allen, S. (2005). Enhanced removal of organic matter and ammoniacal-nitrogen in a column experiment of tidal flow constructed wetland system. J. Biotechnol. *115*(2), 189-197.

Tanner, C.C., Clayton, J.S., Upsdell, M.P. (1995a). Effect of loading rate and planting on treatment of dairy farm wastewaters in constructed wetlands-I. Removal of oxygen demand, suspended solids and faecal coliforms. Wat. Res. *29*(1), 17-26.

Tanner, C.C., Clayton, J.S., Upsdell, M.P. (1995b). Effect of loading rate and planting on treatment of dairy farm wastewaters in constructed wetlands-II. Removal of nitrogen and phosphorus. Wat. Res. *29*(1), 27-34.

Tanner, C.C., D'Eugenio, J., McBride, G.B., Sukias, J.P.S, Thompson, K. (1999). Effect of water level fluctuation on nitrogen removal from constructed wetland mesocosms. Ecol. Eng. *12*(1-2), 67-92.

Tanner, C.C., Sukias, J.P.S., Upsdell, M.P. (1998). Relationships between Loading Rates and Pollutant Removal during Maturation of Gravel-Bed Constructed Wetlands. J. Environ. Qual. *27*(2), 448-458.

Tennessee Valley Authority (TVA), Water Management Resources Group. (1993). General Design, Construction, and Operation Guidelines: Constructed Wetlands Wastewater Treatment Systems for Small Users Including Individual Residences. (2nd ed.). TVA/WM-93/10.

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

Veneman, P.L.M., Pickering, E.W. (1983). Salt bridge for field redox measurements. Soil Sci. Plant Anal. *14(8)*, 669-677.

WERF. (2006). Small Scale Constructed Wetlands Treatment Systems: Feasibility, Design Criteria, and O&M requirements. Wallace, S.D. and Knight, R.L. (Eds.) Water Environment Research Foundation, Alexandria VA.