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# Effect of water level fluctuation on nitrogen removal from constructed wetland mesocosms

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#### Abstract

Nitrogen removal processes were investigated at three frequencies of water level fluctuation, static, low and high (0, 2 and 6  $d^{-1}$ ), in duplicate gravel-bed constructed wetland mesocosms (0.145 m<sup>3</sup>) with and without plants (Schoenoplectus tabernaemontani). Fluctuation was achieved by temporarily pumping wastewater into a separate tank (total drain time  $\sim$  35 min). Intensive sampling of the mesocosms, batch-fed weekly with ammonium-rich  $(\sim 100 \text{ g m}^{-3} \text{ NH}_{4}\text{-N})$  farm dairy wastewaters, showed rates of chemical oxygen demand (COD) and total Kieldahl nitrogen (TKN) removal increased markedly with fluctuation frequency and in the presence of plants. Nearly complete removal of  $NH_4$ -N was recorded over the 7 day batch period at the highest level of fluctuation, with minimal enhancement by plants. Redox potentials (Eh) at 100 mm depth rose from initial levels of around -100 to > 350 mV and oxidised forms of N (NO<sub>2</sub> and NO<sub>3</sub>) increased to ~40 g m<sup>-3</sup>, suggesting conditions were conducive to microbial nitrification at this level of fluctuation. In the unplanted mesocosms with low or zero fluctuation, mean NH<sub>4</sub>-N removals were only 28 and 10%, respectively, and redox potentials in the media remained low for a substantial part of the batch periods (mid-batch Eh  $\sim +100$  and -100 mV, respectively). In the presence of wetland plants, mean NH<sub>4</sub>-N removal in the mesocosms with low or zero fluctuation rose to 71 and 54%, respectively, and COD removal (>70%) and redox potential (mid-batch Eh > 200 mV) were markedly higher than in the unplanted mesocosms. Negligible increases in oxidised N were recorded at these fluctuation frequencies, but total nitrogen levels

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declined at mean rates of 2.4 and 1.8 g m<sup>-2</sup> d<sup>-1</sup>, respectively. NH<sub>4</sub>-N removal from the bulk water in the mesocosms was well described ( $R^2 = 0.97-0.99$ ) by a sorption-plant uptake-microbial model. First-order volumetric removal rate constants ( $k_v$ ) rose with increasing fluctuation frequency from 0.026 to 0.46 d<sup>-1</sup> without plants and from 0.042 to 0.62 d<sup>-1</sup> with plants. As fluctuation frequency increased, reversible sorption of NH<sub>4</sub>-N to the media, and associated biofilms and organic matter, became an increasingly important moderator of bulk water concentrations during the batch periods. TN mass balances for the full batch periods suggested that measured plant uptake estimates of between 0.52 and 1.07 g N m<sup>-2</sup> d<sup>-1</sup> (inversely related to fluctuation frequency) could fully account for the increased overall removal of TN recorded in the planted systems. By difference, microbial nitrification-denitrification losses were therefore estimated to be approximately doubled by low-level fluctuation from 0.7 to 1.4 g N m<sup>-2</sup> d<sup>-1</sup> (both with and without plants), rising to a maximum rate of 2.1 g N m<sup>-2</sup> d<sup>-1</sup> at high fluctuation, in the absence of competitive uptake by plants. © 1999 Elsevier Science B.V. All rights reserved.

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#### 1. Introduction

The nitrogen removal performance of subsurface-flow (SSF) constructed wetlands treating ammonium-rich wastewaters is often relatively poor and has proven difficult to accurately predict (Brix and Schierup, 1990; Knight et al., 1993; Hammer and Knight, 1994; Reed and Brown, 1995). Sequential microbial nitrification-denitrification is generally the main means of ammoniacal nitrogen (NH<sub>4</sub>-N) removal in these wetland systems, with high respiratory oxygen demand and restricted reaeration of the saturated sediments making nitrification the rate-limiting step (Bowmer, 1987; Brix and Schierup, 1990). Aerobic conditions necessary for nitrifiers to develop and function in the substrata of subsurface-flow constructed wetlands are likely to be restricted to surface layers of the gravel, sludge and litter, and the root-zone of wetland plants (Reddy and Patrick, 1984; Reddy et al., 1989a,b).

Although wetland plants can enhance  $NH_4$ -N removal in SSF wetlands operating at appropriate loading rates (Gersberg et al., 1986; Tanner et al., 1995), their relatively low root-zone oxygen release rates seriously limit potential rates of nitrification. In addition to the use of nitrifying pretreatment stages before wetland systems (Gersberg et al., 1983; van Oostrom and Russell, 1994), a variety of approaches to physically promote aeration have been suggested and on trial recently. These include: direct bed aeration (Davies and Hart, 1990), intermittently flooded vertical-flow beds (Burka and Lawrence, 1990; Watson and Danzig, 1993; Green et al., 1997; Laber et al., 1997; von Felde and Kunst, 1997), and alternately or batch-flooded horizontal-flow beds (Brix and Schierup, 1990; Busnardo et al., 1992; Burgoon et al., 1995; Sikora et al., 1995). Alternate periods of drainage and flooding are known to increase N losses from natural wetlands and rice paddies (Patrick and Wyatt, 1964; Reddy and Patrick, 1975), and from tidal marshes (Nuttle and Hemond, 1988), primarily by stimulating organic N mineralisation and nitrification. We hypothesised for gravel-bed constructed wetlands that:

- 1. Both increased fluctuation frequency and plant root-zone oxygen release would enhance microbial oxidation of chemical oxygen demand (COD) and reduced forms of N (ammoniacal and organic) in gravel-bed constructed wetlands;
- 2. Under drained conditions the quantity of  $NH_4$ -N that could be retained within the relatively thin biofilm (30–40  $\mu$ m), adsorbed to gravel surfaces and detritus, and in 'adhering' water films would be limited. Gaseous oxygen entering the interstitial spaces in the gravel matrix would therefore be likely to rapidly penetrate these films, resulting in rapid utilisation of available C and N substrates by aerobes. Conversely the amount of oxygen able to be stored in these films or entrained during reflooding would be small relative to the oxygen demand of the wastewaters being treated, leading to rapid resumption of anaerobic conditions once flooded. Thus, we reasoned that frequent short-duration drainage periods would be required to provide conditions conducive to microbial nitrification in these systems.

Burgoon et al. (1995) invoked a similar rationale to account for the lack of enhancement of biochemical oxygen demand (BOD) and  $NH_4$ -N removal in their batch-fed mesocosms (drained at 3 or 6 day intervals) compared with equivalent continuous-flow (constant water level) systems.

In initial experiments with batch-fed gravel-bed wetland mesocosms, investigating nitrogen removal in the absence of plants at fluctuation frequencies of 0, 4, 8 and  $16 d^{-1}$  (three mesocosms per treatment), we found fluctuations >4 d<sup>-1</sup> resulted in substantial enhancement of NH<sub>4</sub>-N and COD removal (results summarised in McBride and Tanner, submitted). Bioassays of the biofilm-coated gravel media from the mesocosms showed markedly enhanced nitrification potential relative to controls (Nielsen, 1993; Rasmussen, 1993). The objective of the present study was to evaluate the effect of frequency of short duration drain periods on removal of COD, ammonium and total N from an ammonium-rich wastewater, in both the presence and absence of wetland plants, using batch-fed gravel-bed wetland mesocosms.

# 2. Methods

## 2.1. Wetland mesocosms

Experiments were carried out at Ruakura Research Centre, Hamilton, North Island, New Zealand (37° 47′ S, 175° 19′ E), in 12 circular 0.190 m<sup>3</sup> polyethylene tanks (0.238 m<sup>2</sup> × 0.8 m depth; Fig. 1) arranged in a single east-west row, under a clear horticultural plastic shelter ( $\sim$  70% transmission of photosynthetically active radiation). The tanks were filled to 0.59 m depth ( $\sim$  0.145 m<sup>3</sup>) with 14–22 mm

diameter crushed greywacke gravel with an initial effective porosity of 45.3%. An inflow pipe (PVC, 20 mm ID) and three sampling tubes (PVC, 15 mm ID) extended to the bottom of the tanks. A surface outflow set at a height of 0.57 m determined the top of the water level in the tanks, giving a flooded volume of 0.140 m<sup>3</sup> with an initial interstitial water volume of 0.062 m<sup>3</sup>.

Fluctuation treatments were performed by pumping water from the base of mesocosm tanks (12 min) into a covered holding tank, retaining for 10 min, and then allowing it to flow back into the mesocosms via a solonoid valve (8–10 min). Care was taken to reduce the potential for splashing and turbulence, which could have artificially increased aeration of the drained wastewaters during this operation. Operation of the drain–refill cycle (complete duration  $\sim 35$  min) was controlled by



Fig. 1. Diagram of experimental gravel-bed wetland mesocosm (plants not shown) and associated holding tank and sampling tubes. An automated switching system controlled the operation of the pump and solonoid valve, causing the water in the gravel-bed mesocosm to be periodically pumped into the storage tank, then held for 10 min before being allowed to drain back into the mesocosm.

an automated switching device. The exterior of the mesocosms and holding tanks were painted white to reduce radiative heating.

Initial experiments in the unplanted mesocosms at four fluctuation frequencies ranging between 0 and 16 d<sup>-1</sup> (n = 3) were carried out between September and November 1993 (Nielsen, 1993; Rasmussen, 1993). In December 1993 (southern hemisphere summer), six of the tanks (all treatments randomly assigned) were planted with vegetative propagules of *Schoenoplectus tabernaemontani* (C.C. Gmelin) Palla collected from a natural population on the shores of the Waikato River at Hamilton. This species, which has been widely used in constructed wetlands in North America and Australasia (Tanner, 1996), has previously been widely referred to as *Schoenoplectus validus* or *Scirpus validus*, (Smith, 1995). Plant growth was maintained within the confines of the tank area, and side-lighting reduced to simulate shading from surrounding plants, using horticultural shade cloth (50% reduction in photosynthetically active radiation) secured to four vertical fibreglass poles attached to the outside of the tanks. The shade cloth was raised gradually as the plants grew, to maintain it at approximately two thirds of the mean canopy height.

The mesocosms were then fed weekly with farm dairy wastewaters pretreated in a two-stage waste stabilisation pond system (establishment period wastewater, Table 1). In August 1994, before the second growing season, three different treatments of zero (static), two and six fluctuations per day were initiated in duplicate planted and unplanted mesocosms. Preliminary experiments with the planted and unplanted mesocosms were carried out after an 8 week acclimation period (D'Eugenio, 1996). Because of the addition of mechanical aerators to the facultative pond from which the influent wastewaters were being sourced at this time (to meet regulatory requirements), the influent wastewater was changed to that discharging from the upstream anaerobic pond. The experiments reported in the present paper were then carried out after a further acclimation period of 5 weeks with this higher-strength influent (experimental period wastewater, Table 1), during mid summer (24 January-21 February 1995). The mean daily air temperature was 20.1°C (mean range, 15.1–25.2) and mean solar radiation 18.6 + 6.2 MJ m<sup>-2</sup> d<sup>-1</sup> over the period (Ruakura Meteorological Station,  $\sim 150$  m from the experimental site).

# 2.2. Wastewater addition, sampling and analysis

Fresh wastewater was collected each week, transported to the site in large tanks, allowed to settle overnight, and then added slowly to the mesocosms via the influent pipes (Fig. 1), immediately after draining the previous batch of wastewater. Thus, the 'static' mesocosm also received a single fluctuation at the beginning of each batch. To compensate for evapotranspiration losses during batch periods, water levels were adjusted each day by addition of tap water (Hamilton city supply; pH 8.4, alkalinity 0.8 eq m<sup>-3</sup>, conductivity 18.6 ms m<sup>-1</sup>, NH<sub>4</sub>-N < 0.01 g m<sup>-3</sup>, NO<sub>3</sub>-N < 1 g m<sup>-3</sup>), which, during the experimental period, was bubbled with oxygen-free nitrogen gas to reduce dissolved oxygen levels below 2 g m<sup>-3</sup>.

Table 1
Summary of mean constituent concentrations in the influent wastewaters, their mean concentrations in the mesocosms at the beginning and end of 7-day batch loading
periods, and their calculated areal mass loading and removal rates <sup>a</sup>

Constituent	Influent wastew	ater	Mesocosm wa	ters					
	Establishment period	Experimental period	Initial <sup>b</sup>	Final					
				Static		Low fluctuat	uo	High fluctua	tion
				Planted	Unplanted	Planted	Unplanted	Planted	Unplanted
COD Concentration (g m <sup>-3</sup> )	$240 \pm 23$	$605 \pm 70$	$603 \pm 10$	$178 \pm 24$	$275 \pm 29$	$173 \pm 40$	$260 \pm 37$	$142 \pm 24$	$158 \pm 19$
Loading/removal rate (g m <sup>-2</sup> d <sup>-1</sup> ) Percentage removal	* *	 * *	$19.\overline{0}, 20.2$	13.4 71	11.0 54	13.6 71	11.5 57	14.6 77	14.9 74
Soluble CBOD Concentration (g m <sup>-3</sup> )	*	54.5 ± 9.8	*	<b>6.9</b> ± <b>3.0</b>	$15.5 \pm 3.5$	5.9 ± 2.5	$16.5 \pm 3.5$	$3.4 \pm 0.6$	$4.5 \pm 1.8$
<i>CBOD</i> Concentration (g m <sup>-3</sup> ) Loading/removal rate (g m <sup>-2</sup> d <sup>-1</sup> ) Percentage removal	31±9.0 *	77 ± 19.4 *	$74 \pm 21.1$ 2.3, 2.5 *	8.2 ± 1.2 2.1 89	17 ± 1.4 1.9 77	9.2 ± 0.6 2.1 88	$19.5 \pm 0.7$ 1.9 75	$6.0 \pm 1.1$ 2.2 92	$6.7 \pm 1.3$ 2.3 91
<i>NBOD</i> Concentration (g m <sup>-3</sup> ) Loading/removal rate (g m <sup>-2</sup> d <sup>-1</sup> ) Percentage removal	377±61 *	451 ± 38 *	$463 \pm 61 \\ 14.6, 15.5 \\ *$	$\begin{array}{c} 221\pm 69\\ 7.7\\ 52\end{array}$	382 ± 39 2.7 18	112 ± 21 10.9 74	304 ± 48 5.4 35	$3.5 \pm 1.3$ 14.5 99	34 ± 17 14.3 93
<i>TOD</i> Concentration (g m <sup>-3</sup> ) Loading/removal rate (g m <sup>-2</sup> d <sup>-1</sup> ) Percentage removal	618±65 *	$1056 \pm 80$ *	$1058 \pm 61 \\ 33.4, 35.4 \\ *$	$395 \pm 73$ 20.9 63	$650 \pm 49$ 13.6 39	291 $\pm$ 45 24.2 73	558±61 16.7 47	145 ± 24 28.8 86	$192 \pm 26 \\ 29.0 \\ 82$

Constituent	Influent wastew	/ater	Mesocosm wa	ters					
	Establishment period	Experimental period	Initial <sup>b</sup>	Final					
				Static		Low fluctuat	ion	High fluctuat	ion
				Planted	Unplanted	Planted	Unplanted	Planted	Unplanted
<i>TN</i> Concentration (g m <sup>-3</sup> ) Loading/removal rate (g m <sup>-2</sup> d <sup>-1</sup> ) Percentage removal	92.1 ± 14 *	111 * * *	$113 \pm 10.6$ 3.6, 3.8 *	$56.2 \pm 16.0$ 1.8 50	$93.3 \pm 9.1$ 0.7 17	$38.4 \pm 5.5$ 2.4 66	$75.3 \pm 11.0$ 1.3 33	$45.7 \pm 4.5$ 2.1 60	$50.5 \pm 6.2$ 2.1 55
TKN Concentration (g m <sup>-3</sup> )	$90 \pm 14$	$109 \pm 8.8$	$112 \pm 14$	$56.0 \pm 16.0$	$93.3 \pm 9.1$	32.6 ± 4.8	75 ± 11.0	$5.7\pm0.3$	$12.7 \pm 4.0$
Loading/removal rate (g $m^{-2} d^{-1}$ ) Percentage removal	* *	(0 = 0) *	3.5, 3.8 *	1.8 50	0.6 17	2.5 71	1.2 33	3.4 95	3.3 89
$NH_{4}$ - $N$ Concentration (g m <sup>-3</sup> ) Loading/removal rate (g m <sup>-2</sup> d <sup>-1</sup> ) Percentage removal	71 ± 3.0 *	107 ± 6.0 *	97 ± 3.8 3.1, 3.2 *	44.3 ± 3.1 1.7 54	$87.8 \pm 3.3$ 0.3 10	27.7 ± 3.2 2.2 71	$70.3 \pm 8.9$ 0.9 28	$\begin{array}{c} 0.8 \pm 0.4 \\ 3.0 \\ 99 \end{array}$	$7.5 \pm 3.0$ 3.0 92
$NO_{3.}N^c$ Concentration (g m <sup>-3</sup> )	<2	<2	<2	<2	<2	<b>4.8</b> ± <b>2.6</b>	<2	$35.4 \pm 4.4$	$36.7\pm6.0$
$NO_{x}$ - $N$ Concentration (g m <sup>-3</sup> ) Loading/removal rate (g m <sup>-2</sup> d <sup>-1</sup> ) Percentage removal	1.8±1.2 *	$0.85 \pm 0.98$ *	$\begin{array}{c} 0.77 \pm 0.9 \\ 0.024,  0.026 \\ * \end{array}$	$0.2 \pm 0.2 \\ 0.02 \\ *$	$\begin{array}{c} 0.04\pm 0.03\ 0.02\ * \end{array}$	$3.8 \pm 2.7$ -0.10	$0.3 \pm 0.2 \\ 0.02 \\ *$	$40.0 \pm 4.5$ -1.24 *	$37.8 \pm 4.7$ -1.24
<i>TP</i> Concentration (g m <sup>-3</sup> ) Loading/removal rate (g m <sup>-2</sup> d <sup>-1</sup> ) Percentage removal	$14\pm0.6$	19±0.8 *	$18.9 \pm 0.83 \\ 0.60,  0.63$	$12.8 \pm 2.41$ 0.19 34	$19.2 \pm 1.13 \\ -0.01 \\ -2$	$\begin{array}{c} 13.0 \pm 1.56 \\ 0.19 \\ 31 \end{array}$	$19.4 \pm 2.26 \\ -0.02 \\ -3$	$14.1 \pm 1.27$ 0.15 25	$17 \pm 1.06$ 0.06 10

Table 1 (Continued)

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Constituent	Influent wastew	ater	Mesocosm w	/aters					
	Establishment period	Experimental period	Initial <sup>b</sup>	Final					
				Static		Low fluctuation	uo	High fluctuat	ion
				Planted	Unplanted	Planted	Unplanted	Planted	Unplanted
SS									
Concentration (g $m^{-3}$ )	$31 \pm 6$	$160 \pm 23$	$161 \pm 23.0$	$28.0 \pm 2.8$	$35.5\pm12.0$	$20.5\pm7.8$	$23.0 \pm 1.4$	$19.0 \pm 5.7$	$15.0 \pm 4.2$
Loading/removal rate (g $m^{-2} d^{-1}$ )	*	*	5.1, 5.4	4.2	4.2	4.4	4.6	4.5	4.9
Percentage removal	*	*	*	83	78	87	86	88	16
Alkalinity									
Concentration (eq $m^-3$ )	$8.5 \pm 0.6$	$12.9 \pm 0.8$	$12.9 \pm 0.8$	$8.2 \pm 0.57$	$11.8 \pm 0.28$	$5.9 \pm 0.14$	$10.4 \pm 0.57$	1.1 + 0.20	$1.84 \pm 0.11$
Loading/removal rate (eq $m^{-2} d^{-1}$ )	*	۱ <sub>*</sub>	0.41, 0.43	0.15	0.04	0.22	0.08	0.37	0.37
Percentage removal	*	*	*	36	6	54	19	92	86
Conductinity									
Intensity (mS m <sup><math>-1</math></sup> )	$127.8 \pm 3.1$	$184.6 \pm 7.3$	$182 \pm 1.5$	$125.7 \pm 4.7$	$172.6 \pm 3.2$	$104.6 \pm 4.9$	$157.0 \pm 7.7$	86.8 + 3.0	$104.9 \pm 2.7$
Loading/removal rate (mS $d^{-1}$ )	۰.	۱ *	5.7, 6.1	1.75	$0.31^{-}$	2.44	$0.83^{-1}$	3.00	2.57
Percentage removal	*	*	*	31	5	43	14	52	42
Hd	$7.55\pm0.06$	$7.04\pm0.18$	6.75-7.00	$7.45\pm0.09$	$7.11\pm0.02$	$7.20\pm0.06$	$7.63\pm0.13$	$6.59 \pm 0.19$	$6.98\pm0.13$
Redox potential (Eh, mV)	*	-105 (n=2)	*	$276 \pm 24.4$	$-32 \pm 31.3$	$324 \pm 30.4$	$235 \pm 38.9$	$422 \pm 43.9$	$375 \pm 32.1$
Evapotranspiration $(mm \ d^{-1})$	*	*	*	$17.9 \pm 2.5$	$0.8\pm0.4$	$15.1 \pm 2.1$	$0.9\pm0.4$	$11.9 \pm 2.8$	$1.3 \pm 0.4$
<sup>a</sup> Roots, rhizomes and stem bases rec	luced interstitial	volumes in the p	lanted mesoc	osms by ~6%	compared to	those in the	unplanted me	socosms. All e	concentrations

given (unless noted otherwise) are means for two sequential batches of duplicate mesocosms ± 1 S.D. <sup>b</sup> Mean concentrations for all mesocosms, with respective values for areal mass loadings of planted and unplanted mesocosms listed sequentially. <sup>c</sup> Proximate analysis by ion selective electrode. \* Not applicable or value not measured.

Table 1 (Continued)

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Depth-integrated water samples were obtained daily from the mesocosms (after pre-adjustment of water levels) by slowly inserting a stainless steel tube into the two perforated sampling tubes set in the gravel media (Fig. 1). A rubber bung attached to a fine stainless steel wire passing up through the centre of the inserted tube, was used to enclose the sample within the tube. These, and duplicate samples of the wastewaters added at the beginning of each batch, were analysed (all methods APHA, 1989: unless otherwise noted) daily for chemical oxygen demand (COD: dichromate/sulphuric acid digestion, colorimetry); daily and 8 h after batch loading for ammoniacal nitrogen (NH<sub>4</sub>-N; ammonia-selective electrode, Orion model 93-12, Orion Research, Boston, MA) and proximate nitrate nitrogen (NO<sub>2</sub>-N; nitrate-selective electrode. Orion model 93-07 with model 90-02-00 double junction reference electrode). Daily water temperature, conductivity, and pH measurements were made with a Solomat MPM 2000 meter with appropriate modumeters. (Solomat, Stamford, CT); and/or an Orion model 290A meter, which were also used for ion selective and redox potential measurements (see below). Samples from the beginning of each batch (immediately after addition), and 1, 3, and 7 days through the batch periods were analysed for total Kjeldahl nitrogen (TKN, Kjeldahl digestion, phenol/hypochlorite colorimetry), and total oxidised nitrogen (NO<sub>x</sub>-N; cadmium reduction, colorimetry); and at the beginning and end of each batch for total and soluble (GFC filtered) carbonaceous biochemical oxygen demand (CBOD; unseeded, nitrification inhibited), suspended solids (gravimetric, GFC filtered), total phosphorus (persulphate digestion, molybdenum blue colorimetry, NWASCO, 1982). Total nitrogen (TN) was calculated as the sum of TKN and NO<sub>x</sub>-N, organic N as TKN less NH<sub>4</sub>-N, nitrogenous oxygen demand (NBOD) as 4.25 times the sum of NH<sub>4</sub>-N and mineralisable organic N (Henze et al., 1995), and total oxygen demand (TOD) as the sum of COD and NBOD.

First-order volumetric removal rate constants (k), assuming exponential removal to non-zero background concentrations  $(C^*)$  and complete mixing, were calculated for COD removal. Fitted values of  $k_v$  and  $C^*$ , were derived from the following equation (rearrangement of equation 9.153b, Kadlec and Knight, 1996 p. 354), using the general curve-fitting procedure (Levenberg–Marquardt algorithm), weighted by sample standard deviation, of KaleidaGraph (version 3.0, Synergy Software, Reading PA):

$$C_{\rm out} = C^* + [(C_{\rm in} - C^*)e^{-k_{\rm v}t}]$$
<sup>(1)</sup>

where  $C_{out}$ , outflow pollutant concentration (g m<sup>-3</sup>);  $C_{in}$ , influent pollutant concentration (g m<sup>-3</sup>);  $C^*$ , background pollutant concentration (g m<sup>-3</sup>);  $k_v$ , first order volumetric removal rate constant (d<sup>-1</sup>); t, time (days).

This simple model was inappropriate for application to  $NH_4$ -N removal data, because of the importance of reversible sorption to media-surfaces, biofilms and organic matter during the batch cycle and, in the planted systems, ongoing uptake and accumulation by plants. A sorption-plant uptake-microbial model suggested by Kadlec (personal communication, 1997) was therefore applied, where sorption was taken to be the sum of all storage associated with the gravel media and to be describable by reversible Freundlich isotherm kinetics. Mean plant uptake rates, measured during the experimental period (see later) were assumed to be linear (zero order) during the batch periods. A Fortran-based transient model employing fourth order Runge–Kutta integration was developed, which was run on a personal computer. This accounted for mixing of new wastewater additions with water remaining in the drained mesocosms and solved the following equations, comparing predictions against the experimental results.

$$\frac{d(VC_{1})}{dt} = -k_{2}Va_{v}\left[C_{1} - \left(\frac{C_{s}}{K}\right)^{1/m}\right] - Vk_{v}\left(C_{1} - C^{*}\right) - AG$$
(2)

$$\frac{\mathrm{d}(MC_{\mathrm{s}})}{\mathrm{d}t} = +k_2 V a_{\mathrm{v}} \left[ C_1 - \frac{C_{\mathrm{s}}}{K}^{1/m} \right]$$
(3)

where  $a_v$ , media surface area per water volume (m<sup>2</sup> m<sup>-3</sup>); A, wetland surface area (m<sup>2</sup>); V, wetland water volume (l);  $C_1$ , liquid concentration (g m<sup>-3</sup>);  $C_s$ , sorbed concentration on the gravel media (mg N kg (media)<sup>-1</sup>); G, nitrogen requirement for plant growth (mg m<sup>-2</sup> d<sup>-1</sup>);  $k_2$ , first order volumetric transfer rate constant (m d<sup>-1</sup>); K, solid/liquid partition coefficient (l (wastewater) kg (media)<sup>-1</sup>); m, Fre-undlich exponent; M, media mass (kg).

The model was run for 12 consecutive weeks with 20 time steps  $h^{-1}$  and an initial solids NH<sub>4</sub>-N concentration of 20 mg kg (solids)<sup>-1</sup>. It was initially calibrated for the static unplanted mesocosm using  $C^* = 0$  for NH<sub>4</sub>-N, as proposed by Kadlec and Knight (1996), and a NH<sub>4</sub>-N sorption isotherm (m = 0.5) similar to that reported for pea gravel by Sikora et al. (1995). The three remaining coefficients K,  $k_2a_v$  and  $k_v$  were adjusted to give a best fit (minimum sum of squared errors). The model was then applied to the results for the other experimental treatments by adjusting  $k_v$ , and applying appropriate plant N uptake rates and interstitial water volumes, whilst keeping all other values constant

During the final batch, immediately after the main sampling period, interstitial water samples were extracted daily and from 100 mm depth within the mesocosms via in situ sampling tubes (Fig. 1, described in detail in Tanner, 1994a). A dual manifold was used to remove standing water from the sampling tubes before samples were drawn into 60 ml plastic syringes. These were immediately injected into custom-built glass chambers (120 ml), magnetically stirred, and flushed continuously with oxygen-free nitrogen. Measurements were made of redox potential (combination platinum and Ag|AgCl reference electrode, Orion model 96-78) and dissolved oxygen (Yellow Springs Instruments, model 54 A meter, Clark-type electrode zeroed against oxygen-free nitrogen, calibrated in water-saturated air). Redox readings were made after 2 min equilibration using duplicate platinum electrodes, cleaned regularly with fine abrasive and standardised with each other and against a ferrous-ferric standard (Light, 1972). Redox potentials are expressed relative to the standard hydrogen electrode (Eh).

# 2.3. Plant sampling

Shoot densities and total (cumulative) length were determined as a non-destruc-

tive measure of plant growth during the experimental period (final 6 weeks) using techniques previously developed for this morphologically-simple plant (Tanner, 1994a). The number of shoot tips were counted in 150 mm height classes using a multi-tiered quadrat clamped to the tank walls and these values multiplied by their mid-point heights to estimate the total shoot length. At the end of the trial, shoots were cut at the gravel surface, and their bases washed to remove any adhering sediments before sorting into 150 mm height classes using a compartmentalised measuring tray, and counting. Each tank was then excavated and the gravel sorted and wet-sieved (2 mm mesh) to recover below-ground plant material. After further washing and soaking in tap water for 30 min to release loosely bound nutrients: representative subsamples were removed and sorted to determine the relative biomass of rhizomes (including below-ground culm bases) and roots. All above and below-ground tissue samples were then weighed after drving to constant weight in a forced draft oven at 80°C. Subsamples of live and dead shoots, inflorescences, roots and rhizomes from each mesocosm were then ground and analysed for N and P after Kjeldahl digestion (salicylic acid modification with selenium catalyst) using automated methods (Basson, 1976). Allometric relationships between total shoot length, and plant biomass and nutrient accumulation for each mesocosm at the end of the trial were applied to measurements of total shoot length at the beginning of the experimental period to estimate (by difference) rates of plant N and P uptake over the experimental period.

# 2.4. Media sampling

The effective interstitial volume of the mesocosms was measured at the beginning and end of the final 12 weeks of the experimental period to enable mass balances to be calculated, and to determine the effect of plant roots and rhizomes, and biofilm and detritus accumulation on void space in the gravel. After complete draining, the volume of wastewater required to fill the mesocosms to the height of the outflow pipes was carefully measured. At the end of the trial, 1 l subsamples of gravel and associated biofilms and detritus were excavated from depths of 150-300 and 400-450 mm. These were dried to constant weight at  $80^{\circ}$ C in a forced draft oven and weighed before analysis of the non-gravel fraction for TKN and TP (as for plant samples).

# 3. Results

Characteristics of the influent and effluent wastewater are summarised in Table 1. The responses of the duplicate mesocosms tested for each fluctuation treatment were very similar for both batches monitored (see standard deviations given in Table 1), so only overall mean values are shown on the figures to aid clarity.



Fig. 2. Effects of three frequencies of water level fluctuation (static, low and high) on mean redox potential at 100 mm depth in duplicate planted (solid symbols and lines) and unplanted (open symbols and dashed lines) mesocosms during 7-day batch periods. Approximate zones corresponding to aerobic, anoxic and anaerobic conditions are shown, based on Gambrell and Patrick (1978).

#### 3.1. Physico-chemical conditions

Mean water temperatures measured at mid-depth within the mesocosms were similar for both planted and unplanted mesocosms, with a mean of 22.0°C (19.2–27.1) recorded during the experimental period at 09:00 h. Dissolved oxygen (DO) levels measured within the mesocosms were generally near or below the limits of detection for our measurement system (0.05 g m<sup>-3</sup>). Pumping of the wastewater up into the header tanks during drain periods raised DO to between 0.5 and 1 g m<sup>-3</sup>. After refilling, DO levels in the mesocosms remained elevated (~1–1.5 g m<sup>-3</sup>) for a short period, then dropped back to initial levels after 20–40 min. There was a general trend of increasing amplitude and duration of elevated DO with progress through the batch periods. Highest DO elevations of 2.0–2.5 g m<sup>-3</sup> were recorded for the planted high-fluctuation mesocosms on the last day of the batch periods when COD and NH<sub>4</sub>-N had declined to very low levels.

Mean initial wastewater redox potentials below -100 mV rose gradually over the batch period in all except the static unplanted mesocosms (Fig. 2). Addition of plants or low-fluctuation resulted in redox potentials rising to between 200 and 300 mV, increasing further to between 300 and 450 mV when low-fluctuation and plants were combined or higher levels of fluctuation applied. Wastewater pH generally remained relatively well buffered in all treatments, with all values between 6.4 and 7.8. Alkalinity was consumed to varying degrees depending on treatment, with losses of up to 92% (11.8 eq m<sup>-3</sup>) recorded in the planted high-fluctuation mesocosms over a batch period, compared to only 9% in the unplanted static mesocosms (Table 1).

## 3.2. Oxygen demand

The primary-treated farm dairy wastewater added to the mesocosms was characterised by high oxygen demand (mean initial COD 605 g m<sup>-3</sup>; CBOD<sub>5</sub> 77 g m<sup>-3</sup>) and NH<sub>4</sub>-N concentrations (mean 107 g m<sup>-3</sup>). The latter translated to a initial NBOD (including mineralisable organic N) once mixed in the tanks of 463 g m<sup>-3</sup>, giving a total oxygen demand (TOD; COD + NBOD) for the wastewater of 1058 g m<sup>-3</sup>. The CBOD<sub>5</sub> of the wastewater, of which ~70% was in soluble forms, represented only 12% of the initial COD and 7% of the TOD.

Removal of COD in the wetland mesocosms occurred very rapidly on the first day after new wastewater loading, then continued more gradually over the following 6 days of the batch (Fig. 3). COD removal was lowest in the unplanted static and low-fluctuation mesocosms, with ~ 55% or 11 g COD m<sup>-2</sup> d<sup>-1</sup> removed over the batch period (Table 1). The presence of plants increased overall removal at



Fig. 3. Effects of three frequencies of water level fluctuation (static, low and high) on COD concentrations in planted (solid symbols and lines) and unplanted (open symbols and dashed lines) gravel-bed wetland mesocosms during 7-day batch experiments. Results shown are means for duplicate mesocosms, sampled during two consecutive batch periods. The curves shown are fitted to a  $k - C^*$  model (Eq. (1)). Equation parameters and coefficients of determination are summarised in Table 2.

#### Table 2

Summary of first-order volumetric removal rate constants  $(k_v)$ , background concentrations  $(C^*)$  and coefficients of determination  $(R^2)$  calculated for COD removal in the mesocosms, based on a  $k-C^*$  model

	Unplanted			Planted			
	Static	Low	High	Static	Low	High	
$\overline{k_{\rm v}}$ (d <sup>-1</sup> )	0.572	0.483	0.590	0.372	0.495	0.655	
$C^* (g m^{-3}) R^2$	284 0.93	258 0.98	158 0.98	151 0.98	157 0.99	142 0.99	

these fluctuation levels to about 70% or 14 g COD m<sup>-2</sup> d<sup>-1</sup>. Slightly higher COD removals of ~75% or 15 g COD m<sup>-2</sup> d<sup>-1</sup> were recorded for the high-fluctuation mesocosms, with little difference between planted and unplanted systems. Final COD concentrations declined to a minimum of 142 g m<sup>-3</sup> (23% of initial) in the high-fluctuation planted mesocosms. Initially, this fraction of the COD was assumed to represent refractory substances, and assigned as the background concentration (*C*\*) for first order  $k - C^*$  modelling of all treatments. However, the fit of the data became increasingly poor with decreasing water level fluctuation (and concomitant COD removal performance). Specifically fitted  $k_v$  and *C*\* parameters for the COD time-concentration data (Table 2) show *C*\* increasing nearly 2-fold over the range of treatments applied.

Removal of TOD (incorporating NBOD) and CBOD<sub>5</sub> (Table 1) showed broadly similar patterns, in relation to the applied treatments, to that described for COD. TOD removal ranged from 39 to 86% or 14 to 29 g m<sup>-2</sup> d<sup>-1</sup>. Low-fluctuation increased TOD removal, relative to the static tanks, by ~3 g m<sup>-2</sup> d<sup>-1</sup>, with or without plants. Presence of plants, in both the static and low-fluctuation mesocosms, was associated with increases in TOD removal of ~7 g m<sup>-2</sup> d<sup>-1</sup>, while at high-fluctuation plant enhancement was negligible.

#### 3.3. Nitrogen

Ammonium-N comprised ~ 86%, organic N 13% and NO<sub>x</sub>-N ~ 1% of TN in the influent wastewater (Table 1). NH<sub>4</sub>-N concentrations showed little reduction over the batch period in the unplanted static mesocosms, with only slight improvement noted with low-level fluctuation (Fig. 4). The presence of plants markedly increased NH<sub>4</sub>-N removal (increase of ~ 1.4 g m<sup>-2</sup> d<sup>-1</sup>) in both static and low-fluctuation mesocosms to 54 and 71% (1.7 and 2.2 g m<sup>-2</sup> d<sup>-1</sup>), respectively, over the batch period. Highest NH<sub>4</sub>-N removals of 92–99% occurred in high-fluctuation mesocosms with similar mass removals (3.0 g m<sup>-2</sup> d<sup>-1</sup>) recorded for both planted and unplanted systems. The fraction of organic N remaining in the high-fluctuation, planted mesocosms at the end of the batch periods (~ 5% of initial TKN) was assumed to represent refractory N, and the organic N lost, assumed to have been mineralised to NH<sub>4</sub>-N (i.e. to contribute to the NBOD). Fitted  $k_v$  values and coefficients of determination for the sorption-plant growthmicrobial model applied to the NH<sub>4</sub>-N data (Table 3) showed microbial removal rates increasing with both fluctuation frequency and in the presence of plants. Model output for all treatments had stabilised after 10–12 weeks operation. The model predicted that the concentration of NH<sub>4</sub>-N sorbed to the media would rise and fall during batches by between ~1 and 6 mg kg<sup>-1</sup>; increasing with fluctuation frequency and presence of plants (Table 3). This would result in the removal of between 4.2 and 25.6 g m<sup>-3</sup> of NH<sub>4</sub>-N from the bulk solution over the initial 2–3 days of the batch periods, which would later be desorbed as concentrations in the bulk water declined due to microbial and plant uptake, and microbial transformation processes.



Fig. 4. Effects of three frequencies of water level fluctuation (static, low and high) on  $NO_3$ -N and  $NH_4$ -N concentrations in planted (solid symbols and lines) and unplanted (open symbols and dashed lines) gravel-bed wetland mesocosms during 7-day batch experiments. Values for  $NO_3$ -N (large symbols) at the middle and end of the batches are also shown, as confirmation of proximate  $NO_3$ -N results. The curves shown for  $NH_4$ -N are fitted to a sorption-plant uptake-microbial model (Eqs. (2) and (3)). Key equation parameters and coefficients of determination are summarised in Table 3.

#### Table 3

Summary of first-order volumetric removal rate constants  $(k_v)$  and coefficients of determination  $(R^2)$  calculated for NH<sub>4</sub>-N removal in the mesocosms for the 12 week experimental period, based on a sorption-plant uptake-microbial model

	Unplanted			Planted		
	Static	Low	High	Static	Low	High
$\frac{1}{k_{v}}$ (d <sup>-1</sup> )	0.026	0.053	0.46	0.042	0.101	0.62
$R^2$	0.99	0.99	0.99	0.99	0.97	0.98
$C_{\rm s}  ({\rm mg \ kg^{-1}})$	28.1-29.3	25.6-27.8	11.6-17.7	20.9-24.7	17.5-21.5	8.4-14.6
$\Delta C_{\rm s} \ ({\rm mg \ kg^{-1}})$	1.1	2.2	6.1	3.8	4.0	6.2
$\Delta C_1 (\text{g m}^{-3})$	4.2	8.6	23.8	15.7	16.5	25.6

The absolute range ( $C_s$ ) and maximum difference ( $\Delta C_s$ ) in NH<sub>4</sub>–N concentration sorbed to the gravel media, and maximum concomitant reduction in NH<sub>4</sub>-N concentration in the bulk solution ( $\Delta C_1$ ) during the final 7 day batch period are given, based on model predictions. Apart from allowance for different interstitial water volumes and plant N uptake in the planted mesocosms, all parameters except  $k_v$  were kept constant for all treatments.

Model parameters values used:  $A = 0.238 \text{ m}^2$ ; V = 52.5 l planted, 55.6 l unplanted; water volume retained in the mesocosm when 'drained' ( $V_{\text{held}}$ ) = 9.2 l; initial  $C_1 = 107 \text{ g m}^{-3}$ ; initial  $C_s = 20 \text{ mg kg}^{-1}$ ;  $C^* = 0$ ; M = 216 kg; K = 3,  $k_2 a_v = 0.8$ ; m = 0.5; G as listed in Table 4.

Oxidised forms of N remained relatively low in the static and low-fluctuation mesocosms with little difference when plants were present, except near the end of the batch period under the low-fluctuation regime, when concentrations rose to 3.8 g m<sup>-3</sup> in the planted mesocosms (Fig. 4). In contrast, NO<sub>3</sub>-N levels rose gradually during the batch periods in both the planted and unplanted high-fluctuation mesocosms, reaching final concentrations of nearly 40 g m<sup>-3</sup>. TN levels (Fig. 5) showed greatest reduction in the low fluctuation planted mesocosms, with 66% or 2.4 g m<sup>-2</sup> d<sup>-1</sup> removal by the end of the batch period. Despite greater reduction in NH<sub>4</sub>-N concentrations in the high-fluctuation mesocosms, gradual accumulation of NO<sub>x</sub>-N stabilised TN removal at 55–60%. Only slightly lower TN removals of ~ 50% were recorded for the planted static mesocosms, but to removals declined to 17% in the equivalent unplanted mesocosms.

#### 3.4. Other key wastewater constituents

SS removal during batch periods ranged between 78 and 91% (4–5 g m<sup>-2</sup> d<sup>-1</sup>) with a general trend of increasing removal with level of fluctuation (Table 1). TP concentrations showed negligible reduction (or slight increases) in the unplanted mesocosms, irrespective of fluctuation treatment, but removals of 25–34% (0.15–0.19 g m<sup>-2</sup> d<sup>-1</sup>) were recorded for the planted systems.





# 3.5. Plant growth responses and nutrient accumulation

Obvious visual differences in the above-ground growth of plants became discernible soon after experimental fluctuation regimes were established. Spring growth of *S. tabernaemontani* was most rapid in the static mesocosms, with darker green, higher density and taller shoots. As well as being less vigorous, plant shoots in the fluctuating mesocosms were noticeably yellow-green in colour. Differences in growth became less pronounced over summer when higher strength wastewaters were applied, but were still apparent at the end of the trial when final sampling was undertaken.

Final mean shoot densities in all mesocosms were all  $\sim 2000 \text{ m}^{-2}$ , while mean total shoot length declined from 2.98 to 2.75 to 1.98 km m<sup>-2</sup>, and total aboveground biomass from 6.36 to 4.27 to 3.31 kg m<sup>-2</sup> with increasing fluctuation frequency. Plant allocation to sexual reproduction also declined with increasing fluctuation, with inflorescence development reducing from 33 to 10 to 6% of shoots and inflorescence biomass reducing from  $\sim 1.04$  to 0.22 to 0.04 kg m<sup>2</sup>. Belowground biomass was very similar for all mesocosms at  $\sim 2$  kg m<sup>-2</sup>, but differences in above-ground growth resulted in the below-to above-ground biomass ratios increasing from 0.32 to 0.50 to 0.57 with increasing fluctuation frequency. Mean plant tissue N (below and above-ground) was 16.5 g kg<sup>-1</sup> in the static and high-fluctuation treatments, increasing to nearly 20 g kg<sup>-1</sup> in the low-fluctuation treatment. Mean tissue P levels were ~ 4.3 g kg<sup>-1</sup> in both fluctuation treatments, reducing to 3.8 g kg<sup>-1</sup> under static conditions. Total (above and below-ground) N and P accumulation by plants showed a general decline with increasing level of fluctuation from a mean of 140 to 126 to 85 g N m<sup>-2</sup> and from 32 to 27 to 22 g  $P m^{-2}$ .

Estimated short-term plant growth rates, and N and P uptake rates during the experimental period showed a similar pattern of decline with increasing fluctuation frequency (Table 4). Plant N uptake estimates for the experimental period (Table 4) represented  $\sim 29$ , 27 and 14%, for the static, low and high fluctuation mesocosms, respectively, of the mass of TN applied at the beginning of each batch (Fig. 5). This was sufficient to fully account for differences in TN removal between the planted and unplanted mesocosms. Plant P uptake estimates for the experimental period (Table 4) were also similar to the differences in TP removal between planted and unplanted mesocosms at all levels of fluctuation.

Rate	Static	Low fluctuation	High fluctuation
Total shoot length increment (m m <sup>-2</sup> d <sup>-1</sup> )	24.2	18.7	6.9
Total biomass increase (g m <sup>-2</sup> d <sup>-1</sup> )	63	50	32
Total plant N uptake (g m <sup>-2</sup> d <sup>-1</sup> )	1.07	0.99	0.52
Total plant P uptake (g m <sup>-2</sup> d <sup>-1</sup> )	0.24	0.22	0.14

Table 4

Estimated mean areal rates of plant growth and nutrient uptake for the planted mesocosms operated at three frequencies of water level fluctuation

## 3.6. Media nutrient accumulation

Final media N and P concentrations did not differ substantially between treatments. Samples from 150–300 mm depth consistently showed lower N and P than those from 400–450 mm ( $25 \pm 6$  and  $64 \pm 16$  mg N kg<sup>-1</sup>;  $62 \pm 23$  and  $94 \pm 11$  mg P kg<sup>-1</sup>, respectively). Mean media accumulation was equivalent to ~ 36 g N m<sup>-2</sup> and 88 g P m<sup>-2</sup>, giving mean accumulation rates of 0.089 g N m<sup>-2</sup> d<sup>-1</sup> and 0.22 g P m<sup>-2</sup> d<sup>-1</sup> (assuming linear rates of uptake over the full experimental period). Comparison with recorded removal rates for the mesocosms suggests that media N accumulation was not likely to be a significant removal mechanism during the experimental period. Mean media P accumulation rates were potentially of similar magnitude to plant uptake estimates, however the lack of P removal shown by the unplanted mesocosms (except at high fluctuation) suggests that the P sorption capacity of the media and associated biofilms was likely to have been largely saturated after its initial year of operation.

## 3.7. Hydrology

Evapotranspiration losses from the mesocosms (Table 1) broadly reflected differences in above-ground plant biomass. In the absence of plants, evaporative losses were ~1 mm d<sup>-1</sup>, representing <3 mm d<sup>-1</sup> change in water level in the gravel-filled mesocosms. Plant evapotranspiration at the end of the trial resulted in mean daily losses of ~ 18 mm under static conditions, decreasing to ~ 12 mm with increasing fluctuation. This represents a maximum daily removal of 8% of water volume resulting in a maximum daily water level decrease of ~ 45 mm for the planted mesocosms.

Gradual build-up of solids and biofilm, and, in the planted mesocosms, growth of roots and rhizomes resulted in reductions in the effective void space of the media. This resulted in 5–6% difference between planted and unplanted treatments, in the volume of wastewater being treated within a batch. This was taken into account in all calculations of mass and percentage removal rates, to allow direct performance comparisons to be made between treatments. During the final 12 weeks of the trial, the effective water volume of the unplanted mesocosms declined from  $56.4 \pm 1.65$  to  $55.6 \pm 1.741(40.1-39.6\%)$  effective void space), while that of the planted mesocosms declined from  $53.8 \pm 0.46$  to  $52.5 \pm 1.431(38.3-37.3\%)$  effective void space). By difference, this indicates a final below-ground plant root and rhizome volume of ~  $6.4 \pm 1.591$  kg<sup>-1</sup> of below-ground biomass (on a dry weight basis).

## 4. Discussion

Consistent with our first hypothesis, multiple short duration water level fluctuations markedly increased removal of both COD and TKN from the high-strength agricultural wastes supplied to the gravel-bed wetland mesocosms. Wetland plants also considerably enhanced COD and TKN removal under static and low fluctuation conditions, but only showed a small additional effect at the higher fluctuation frequency tested (6 d<sup>-1</sup>). As found for intermittently loaded vertical flow systems (Burka and Lawrence, 1990; von Felde and Kunst, 1997), COD and TKN removal occurred simultaneously during the batch periods, rather than sequentially as often assumed when designing constructed wetlands for TKN removal (e.g. Reed et al., 1995; Johansen and Brix, 1996). Rhizomes and roots in the planted mesocosms reduced the interstitial water volumes, and hence the mass loadings applied, by 5-6% compared to mesocosms without plants. The magnitude of bulk water concentration differences between the planted and unplanted systems was thus reduced when converted to mass removals per unit of treatment system volume or area.

## 4.1. Fate of nitrogen losses

Plant nutrient uptake  $(0.5-1.1 \text{ g N m}^{-2} \text{ d}^{-1} \text{ and } 0.14-0.24 \text{ g P m}^{-2} \text{ d}^{-1})$  could fully account for differences in TN (and TP) removal between planted and unplanted treatments at equivalent fluctuation levels. The mesocosms had been operating for over a year at this stage, and net accumulation of both N and P in the media appeared to be relatively low or negligible (~0.09 and -0.04 to 0.06 g m<sup>-2</sup> d<sup>-1</sup>, respectively) during the experimental period. Continuing net N accumulation in the media at this time was likely to be primarily due to the gradual accretion of refractory organic matter in the mesocosms (Kadlec and Knight, 1996).

Ammonia volatilisation was not likely to be a major removal mechanism in the mesocosms, because pH generally remained < 7.6, maximum temperatures in the mesocosms were always  $< 30^{\circ}$ C (mean 20.1) and the gravel-covered water surface was protected from wind turbulence (Jayaweera and Mikkelsen, 1991). Small increases in volatilisation losses may, however, have occurred during drain and fill operations in the fluctuating systems. Microbial nitrification-denitrification is generally considered to be the major means of N removal in constructed wetlands (Gersberg et al., 1986; Brix and Schierup, 1990; Hammer and Knight, 1994). Low oxygen availability in the predominantly anaerobic substrata of subsurface-flow systems generally makes nitrification the rate limiting step. Both water level fluctuation and root-zone oxygen release by wetland plants are likely to have increased the oxygen supply to the wetland media, potentially enhancing aerobic decomposition of organic matter (measured as COD in the present study), mineralisation of organic N and nitrification of NH<sub>4</sub>-N (Reddy et al., 1989a,b; Brix and Schierup, 1990; Moore et al., 1992).

Oxidised forms of N accumulated in the high fluctuation mesocosms, reaching final concentrations of > 35 g N m<sup>-3</sup>. This was associated with substantial consumption of alkalinity, characteristic of microbial nitrification (without full subsequent denitrification, Henze et al., 1995). Remaining COD levels in these microcosms were very low by the end of the batch periods, when nitrate started to accumulate, suggesting low organic carbon availability was likely to be limiting further losses via denitrification (Henze et al., 1995). NO<sub>x</sub>-N accumulation was

minimal in the low fluctuation treatments, but substantial losses of TN occurred, exceeding those able to be accounted for by plant and/or media storage. COD reduction was slower in these treatments, providing relatively anoxic conditions and a continuing source of organic carbon during the batch period.  $NO_x$ -N produced under these conditions was likely to have been subsequently lost by denitrification. Denitrification was not measured directly in the mesocosms, but bioassays performed using media excavated from 100–150 mm depth in the mesocosms (nitrous oxide accumulation during anaerobic incubation with added nitrate, using an acetylene block technique) showed substantial denitrification potential (D'Eugenio, 1996).

# 4.2. Enhancement of oxygen supply

COD removal and redox potentials were substantially higher in the presence of plants and at high fluctuation, consistent with greater oxygen (and nitrate) availability in these treatments. Lower COD, particularly in the latter part of the batch periods, would have been expected to have reduced competition from aerobic heterotrophs for available oxygen, enhancing conditions for nitrifiers (Henze et al., 1995). However, mass differences in reduced nitrogen (TKN) reduction between planted and unplanted mesocosms operating at the same level of fluctuation were small  $(0.1-0.3 \text{ gm}^{-2} \text{ d}^{-1})$  when plant uptake and accumulation were taken into account. This suggests that in our experimental system root-zone oxygen release had little overall effect on nitrification rates per unit of mesocosm volume or area, with enhanced TKN removal in the planted mesocosms primarily attributable, instead, to plant uptake and accumulation.

In the absence of plants, low and high water level fluctuations were able to increase apparent TOD removal from the wastewater by ~ 3 and 15 g m<sup>-2</sup> d<sup>-1</sup>, respectively. In the presence of plants, 6–8 g m<sup>-2</sup> d<sup>-1</sup> of additional oxygen demand (based on TOD determinations) was removed from the static and low fluctuation mesocosms, but plants made negligible difference to TOD removal at high fluctuation. If the enhanced NBOD removal in the planted mesocosms (compared to equivalent unplanted systems) was indeed primarily due to plant uptake of NH<sub>4</sub>-N, then only ~ 2 g m<sup>-2</sup> d<sup>-1</sup> of additional oxygen demand (measured as COD) was satisfied in the presence of plants in the static and low fluctuation mesocosms. This is at the lower and most realistic end of the rather wide range of values that have been estimated for wetland plant root-zone oxygen fluxes based on BOD and NH<sub>4</sub>-N disappearance (0–29 g m<sup>-2</sup> d<sup>-1</sup>, Kadlec and Knight, 1996; Table 1). However, it is still about an order of magnitude above fluxes measured by gas exchange techniques in a soil-based, subsurface-flow constructed wetland (Brix and Schierup, 1990).

Estimates of plant root-zone oxygen flux, such as those above (based on COD removal) and most of those summarised by Kadlec and Knight (1996), based on BOD or  $NH_4$ -N removal) assume that removal is predominantly via aerobic processes. However, much of the COD removal recorded in the mesocosms, particularly in the static and low-fluctuation treatments, is likely to be due to

anaerobic processes such as methanogenesis, denitrification and sulphate reduction (Burgoon et al., 1995; Kadlec and Knight, 1996; Tanner et al., 1997). Thus, actual oxygen transport and consumption rates in the wetland media may be substantially overestimated using such indirect techniques.

The biomass of *S. tabernaemontani* growing in the mesocosms at the end of the experiment ( $\sim 5-8$  kg m<sup>-2</sup>) was very high compared to that normally found for this species in larger-scale constructed wetland systems ( $\sim 3-4$  kg m<sup>-2</sup>, Tanner, 1994b). Despite attempting to reduce side-lighting of plants growing in the mesocosms by the use of shade-cloth screens (Section 2.1), edge-effects (Busnardo et al., 1992; Tanner, 1994a) appear to have resulted in atypically high plant growth. This is likely to have increased the magnitude of plant nutrient uptake and the potential for root-zone oxygen release above the normal levels that could be expected in larger-scale systems. The reduced tissue N concentrations and plant growth noted under high fluctuation regimes, suggest that despite the relatively large weekly loadings of N, plants growing under these conditions were out-competed by microbes for available N. Plants growing in natural systems subject to such fluctuations (e.g due to tidal influence) may be subject to similar microbial competition for available N.

## 4.3. Modelling

Kadlec and Knight (1996) have clearly illustrated for constructed and natural wetlands, the generally poor fit of simple first order models that assume exponential decay of contaminants to zero background levels. Instead, they have proposed a first order  $k - C^*$  model that assumes exponential decay to non-zero background concentrations, and have shown how this can be successfully used to describe the contaminant removal patterns generally observed in wetland treatment systems. First order volumetric reaction rates  $(k_{a})$  calculated for COD and NH<sub>4</sub>-N in the present study, increased markedly with increased water level fluctuation and the presence of wetland plants. Background concentrations  $(C^*)$  calculated for COD removal from the unplanted static and low fluctuation mesocosms were considerably higher than those predicted for other more oxic treatments (Table 2). Kadlec and Knight (1996) have defined the background concentration ( $C^*$ ) as the zero order return flux of a contaminant (from biomass, soil and litter within the wetland) divided by  $k_{y}$ . However, for complex organic constituents (measured as part of the COD in the present study) this term presumably also includes the fraction that is not able to be metabolised under the environmental conditions of the system they are being treated in. The differences in  $C^*$  noted in the present study between treatments supplied with the same wastewater, suggest that return fluxes of these constituents and/or their biodegradable fraction varied depending on the environmental conditions (particularly oxygen status) of the treatment system. This presumably reflects differences in the efficacy of the alternative metabolic pathways which occur under different levels of oxygen supply (Moore et al., 1992). It suggests that, for COD, BOD and other measures of complex organic compounds, caution should be exercised when applying generalised values of  $C^*$ 

(Kadlec and Knight, 1996) to systems with different wastewater characteristics, loading regimes and wetland designs.

Initial reductions in  $NH_4$ -N concentrations from the bulk water of the mesocosms were extremely rapid during the first 8 h of the batch periods. At the start of each new batch the  $NH_4$ -N levels sorbed to the biofilm and media surfaces of the mesocosms would have been relatively depleted, due to removal in the previous batch. Thus, part of the rapid initial 'removal' (from the wastewater) observed in these systems is likely to have been due to a combination of reversible physicochemical sorption and microbial assimilation (McBride and Tanner, submitted), with subsequent microbial assimilation and transformation, and plant uptake of desorbed  $NH_4$ -N occurring in the later stages of the batch periods. In studies of similar gravel-bed wetland systems batch-fed with ammonium-rich synthetic wastewaters, Sikora et al. (1995) attributed rapid initial declines in  $NH_4$ -N to reversible sorption by pea gravel. Organic matter associated with biofilms and accumulated solids in the media in the present study is, however, likely to have had substantially higher sorption potential than that of the gravel alone (Decho, 1990; Freeman et al., 1995; Kadlec and Knight, 1996).

We were able to closely mimic the experimental data using a sorption-plant uptake-microbial model, employing the same sorption parameters for all systems. The model was not highly sensitive to the sorption isotherm parameters used. Relatively small increases in reversibly sorbed pools of  $NH_4$ -N in the media were able to describe the rapid initial losses observed in the bulk solution, with subsequent desorption later in the batch period, providing for continuing  $NO_x$ -N production in the high fluctuation systems, when  $NH_4$ -N concentrations in the bulk water were low. It would be useful to determine the size of reversibly sorbed  $NH_4$ -N pool and the sorption isotherm parameters associated with the media, biofilms and accumulated organic matter to further validate the appropriateness of the model used.

# 4.4. Practical application

The results of the present mesocosm study show that TN and COD removal in constructed wetland systems can be substantially enhanced by appropriate water level fluctuation regimes. We have not tried to specifically optimise the performance of our experimental system, but the results suggest that required treatment times could be considerably reduced by increasing the frequency of drainage and decreasing the duration of flooding periods. Utilisation of higher specific surface area media, such as coarse sands, or specialised ammonium-adsorbent media, such as natural zeolites (Green et al., 1996; Nguyen and Tanner, 1998), offer the potential to further enhance nitrogen removal efficiency per fluctuation, by increasing the biofilm surface area and quantity of sorbed substrate (both  $NH_4$ -N and organic compounds) accessible to biofilms during aerobic phases. Modelling approaches, such as those used here and in a companion study (McBride and Tanner, submitted), may be used to assist in the optimisation of bed designs and fluctuation regimes for nitrogen removal from different wastewater types and strengths.

Intermittent aeration of the media was achieved by pumping of water between the constructed wetland and a supplementary reservoir in the present study. On sloping sites, sequential flooding and drainage could be achieved, instead, using a series of terraced gravel-beds, with flow controlled by siphons or automated valves. Alternatively, direct bed aeration (pumping air instead of water) may be a more energy efficient means of achieving the same end, essentially creating a form of aerated submerged biofilter (Henze et al., 1995). Direct aeration was trailed with some success by Davies and Hart (1990) by retrofitting sections of an existing SSF gravel-bed wetland.

Comparison of the results of the present study with those from studies employing other approaches to promote physical aeration of SSF constructed wetlands (e.g. intermittent vertical-flow) is extremely difficult because of differences in wastewater characteristics and the frequent absence of reported flow data, hindering calculation of comparative mass loadings and removals. The main difference in our approach compared to that commonly followed for intermittent vertical-flow systems is the use of relatively short drainage periods to provide intermittent aeration within a predominantly saturated bed, rather than intermittent unsaturated flow (except in the surface layers) followed by longer drainage and rest periods. A potential advantage of our approach is that it does not rely on restricted permeability in the surface layers of the bed to disperse the influent across the bed surface and control infiltration rates, and is thus likely to be less vulnerable to clogging.

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