Evaluation of Constructed Wetland Treatment Performance for Winery Wastewater

Mark E. Grismer, Melanie A. Carr, Heather L. Shepherd

ABSTRACT: Rapid expansion of wineries in rural California during the past three decades has created contamination problems related to winery wastewater treatment and disposal; however, little information is available about performance of on-site treatment systems. Here, the project objective was to determine full-scale, subsurface-flow constructed wetland retention times and treatment performance through assessment of water quality by daily sampling of total dissolved solids, pH, total suspended solids, chemical oxygen demand (COD), tannins, nitrate, ammonium, total Kjeldahl nitrogen, phosphate, sulfate, and sulfide across operating systems for winery wastewater treatment. Measurements were conducted during both the fall crush season of heavy loading and the spring following bottling and racking operations at the winery. Simple decay model coefficients for these constituents as well as COD and tannin removal efficiencies from winery wastewater in bench-scale reactors are also determined. The bench-scale study used upward-flow, inoculated attached-growth (pea-gravel substrate) reactors fed synthetic winery wastewater. Inlet and outlet tracer studies for determination of actual retention times were essential to analyses of treatment performance from an operational subsurface-flow constructed wetland that had been overloaded due to failure to install a pretreatment system for suspended solids removal. Less intensive sampling conducted at a smaller operational winery wastewater constructed wetland that had used pretreatment suspended solids removal and aeration indicated that the constructed wetlands were capable of complete organic load removal from the winery wastewater. *Water Environ. Res.*, **75**, 412 (2003).

KEYWORDS: constructed wetlands, winery wastewater, tracer studies, subsurface flow, degradation modeling.

Introduction

Winery- and brewery-process wastewater differ greatly from domestic wastewater because of high organic concentrations, variable flowrates, limited nutrients, and lack of pathogens (Cronin and Lo, 1998). If not disposed to municipal systems, winery wastewater is typically stored and treated in aerated ponds and may be disposed via postharvest vineyard irrigation. However, with increased production and costs, there has been a move for wineries to treat their wastewater on-site. Wastewater generated from wine or beer production is similar as it results from various processes, including fermentation followed by washing of tanks, barrels, bottles, and so on. However, breweries and wineries have different wastewater treatment concerns and seasonal variations such that the focus here is on winery wastewater treatment only. For example, winery wastewater flows and strength exhibit seasonal fluctuations due to fall harvesting and crush operations. Noting the ability of constructed wetlands to assimilate variable and large organic loadings as well as their low maintenance and operational costs (Etnier and Guterstam, 1997), Shepherd and Grismer (1997) and Larson (1999) asserted that constructed wetlands could be an attractive system for moderately sized wineries. Their application to these more highly concentrated wastewaters has also been explored (e.g., Ronquest and Britz, 1999; Shepherd, 1998; Shepherd et al., 2001a).

Current Research. Rapid expansion of the wine industry in rural California during the past three decades has created environmental contamination problems related to winery wastewater treatment and disposal. However, until recently (e.g., Shepherd et al., 2001a) little research has been conducted characterizing winery wastewater and use of on-site treatment.

Recent reviews (e.g., Carr, 2001; Grismer and Shepherd, 1998; Grismer et al., 1999, 2000; Grismer and co-workers, 2001a) of winery (and related brewery and distillery) wastewater treatment methods have underscored the need for additional research in the United States, particularly of full-scale systems and individual processes. In addition to the pilot-scale constructed wetlands described by Shepherd et al. (2001a), a variety of traditional treatment methods have been applied to winery wastewater treatment with varying success at the bench- or pilot-scale level. In many cases, performance of these systems in the field is uncertain or unknown because of limited testing of extremely variable wastewater flows and quality.

Recent research considering winery wastewater treatment includes evaluation of aerobic and upflow anaerobic sludge bed (UASB) reactors and constructed wetlands. A few of these investigations are briefly reviewed here to illustrate some of the complexities associated with winery wastewater treatment. Using air-bubble column bioreactors with self-adapted microbial populations (either free or immobilized on polyurethane particles or immobilized on Raschig rings in a packed bed), Petroccioli et al. (2000) measured chemical oxygen demand (COD) removal rates from winery wastewater. At loads ranging from 8×10^3 to 11×10^3 mg COD/L and a maximum loading rate of approximately 8800 mg COD/(L·d), the greatest COD removal rate achieved was greater than 90% (6600 mg COD/[L·d]) using free activated sludge in the bubble column bioreactor at a hydraulic retention time (HRT) of approximately 0.8 days. Kalyuzhnyi et al. (2000, 2001a, 2001b) evaluated the start-up and operational performance of two laboratory (2.6-L working volume) UASB reactors treating winery wastewater at strengths of 1×10^3 to 17×10^3 mg COD/L and a range of temperature and loading conditions. Following a 2- to 3-month start-up period, maximum loading rates were 15 900, 6.5×10^3, 12.5×10^3, and 7.2×10^3 mg COD/(L·d) for runs at 35, 19 to 21, 18 to 20, and 4 to 10 °C, respectively, with HRTs of approximately 1 day. Chemical oxygen demand removal rates

Table 1—Constituent methods of analysis.

Constituent	Type of analysis	Accepted Hach method[a]
Ammonium	colormetric (Nessler)	8038
COD	digestion (colormetric)	8000
Nitrate	colormetric	8507
Phosphate	colormetric	8156
Sulfate	turbidimetric	8051
Sulfide	colormetric (methylene blue)	8131
Tannins	colormetric (Folin–Ciocalteau)	–
TKN	colormetric (Nessler)	8038
TSS	gravimetric	8164

[a] APHA et al. (1998).

exceeded 85% for the warmer systems and approximately 60% for the coldest, with substantial decoloration of effluents and reduction of polyphenols (between 45 and 67%) in all cases. When two UASB reactors were operated in series, the average total COD removal exceeded 70% for average loading rates of 2200, 1800, and 1300 mg COD/(L·d) and HRTs of 2 days at 10, 7, and 4 °C, respectively. In an evaluation of a full-scale UASB system at a winery in South Africa, Laubscher et al. (2001) found problems with accumulation of a floating scum layer that on occasion was so severe that it forced a shutdown of the treatment system to enable physical removal of the scum. Attempting to replicate the scum-layer formation in the laboratory, they found that the scum layer developed only with grain distillation wastewater and its severity seemed to depend on the wastewater total suspended solids (TSS) levels. Reducing TSS concentrations by drum filtration, settling, or dilution reduced but did not eliminate scum-layer accumulation, raising questions of the long-term viability of UASB systems for treating distillation wastewaters.

Finally, Shepherd et al. (2001a) evaluated the performance of a pilot-scale subsurface-flow constructed wetlands (6.1 m long × 2.4 m wide × 1.2 m deep) in treating winery wastewater flows ranging from 80 to 170 m^3/d at organic loads of 600 to 45 × 10^3 mg COD/L, and measured average removal rates of 98% for COD and 97% for TSS when combining the constructed wetlands with an upflow sand prefilter. The system also seemed to be effective at neutralizing the pH of the acidic winery wastewater and at removing the limited nitrogen (78.2%) in the wastewater in addition to sulfide (98.5%), orthophosphate (63.3%), volatile fatty acids (99.9%), tannins and lignins (77.9%), and all settleable solids. Grismer and co-workers (2001b) determined the hydraulic characteristics of the pilot-scale constructed wetlands used by Shepherd et al. (2001b) to determine a rate-dependent COD decay coefficient using a retardation-type model. What continues to be lacking is a complete evaluation of the performance of full-scale constructed wetlands or many other types of treatment systems for winery wastewater.

In addition to evaluation of full-scale systems, more information is needed about treatment of particular components of winery wastewater. For example, winery wastewater includes recalcitrant constituents (polyphenols and lignins) that are difficult to degrade because of their structure as well as high molecular weights. Of these, tannins are the most common and crucial to the wine-making process because of their effects on taste, puckering, bouquet, and finish of the wine; biological methods have been developed for their rapid measurement (Jewell and Ebeler, 2001). Tannins, which are most abundant in red wine, can precipitate proteins and act to inhibit microbial digestion (Sarni-Manchado et al., 1999), potentially limiting removal efficiencies. Of the three types of tannins (hydrolyzable, condensed, and catechins), hydrolyzable tannins are the simplest to degrade, while condensed tannins are rarely degraded (Bhat et al., 1998). Catechins exhibit both hydrolyzable and condensed properties. Tannins, however, are sensitive to light degradation, although they require months of exposure, but may adversely affect stream habitat when in high concentrations (Biosystems, 1993). An investigation of the performance of constructed wetlands for treating winery wastewater should include evaluation of the efficacy of recalcitrant compound degradation.

Evaluation of constructed wetland performance in the field requires not only analysis of constituent degradation or transformation, but also a hydraulic assessment of the flow properties of the constructed wetland bed under the variable operating conditions found during actual use so as to improve modeling and design efforts in the field. The overall project objective was to determine full-scale HRTs and treatment performance through assessment of water quality by daily sampling of total dissolved solids (TDS), pH, TSS, COD, tannins, nitrate, ammonium, total Kjeldahl nitrogen (TKN), phosphate, sulfate, and sulfide from two full-scale systems. A secondary goal was to quantify COD and tannin removal rates from winery wastewater in bench-scale reactors. Specifically, the research objectives were to

- Determine and model (i.e., estimate decay constants) tannin removal rates of full-scale constructed wetlands and simple bench-scale pea-gravel reactors;
- Determine and model full-scale treatment efficiencies for TSS, COD, sulfate, sulfide, TKN, nitrate, ammonium, and phosphate; and
- Quantify the difference in treatment of winery wastewater in constructed wetlands during crush and noncrush seasons.

Field Setting and Experimental Methods

Operational, full-scale subsurface-flow constructed wetlands servicing a moderate-production winery near Hopland, California, and a smaller production winery near Glen Ellen, California, were evaluated during the fall harvest–crush and spring seasons. In each case, potassium bromide tracer studies were conducted to determine HRTs during or prior to water quality sampling periods. Water quality sampling was much more intensive at the Hopland facility and included determination of COD and tannin removal rates in the effluent and at several locations along the constructed wetlands. The full-scale designs were scaled-up versions of the pilot-scale system described by Shepherd et al. (2001a), although TSS pretreatment systems differed. Both wastewater treatment systems included solids (e.g., stems, seeds, and skins) removal systems followed by facultative settling ponds prior to discharge to the constructed wetlands; however, the Glen Ellen facility also used a rotary screen TSS removal system before discharge to the facultative pond. At the Hopland facility, clarifiers were also added between the pond and constructed wetlands after this study was completed. The facultative pond at Glen Ellen served as a clarifier, while, at Hopland, the facultative pond was undersized, resulting in excess discharge of suspended solids and organics and subsequent overloading of the constructed wetlands during the study period. Both treatment systems had recirculation capabilities between the

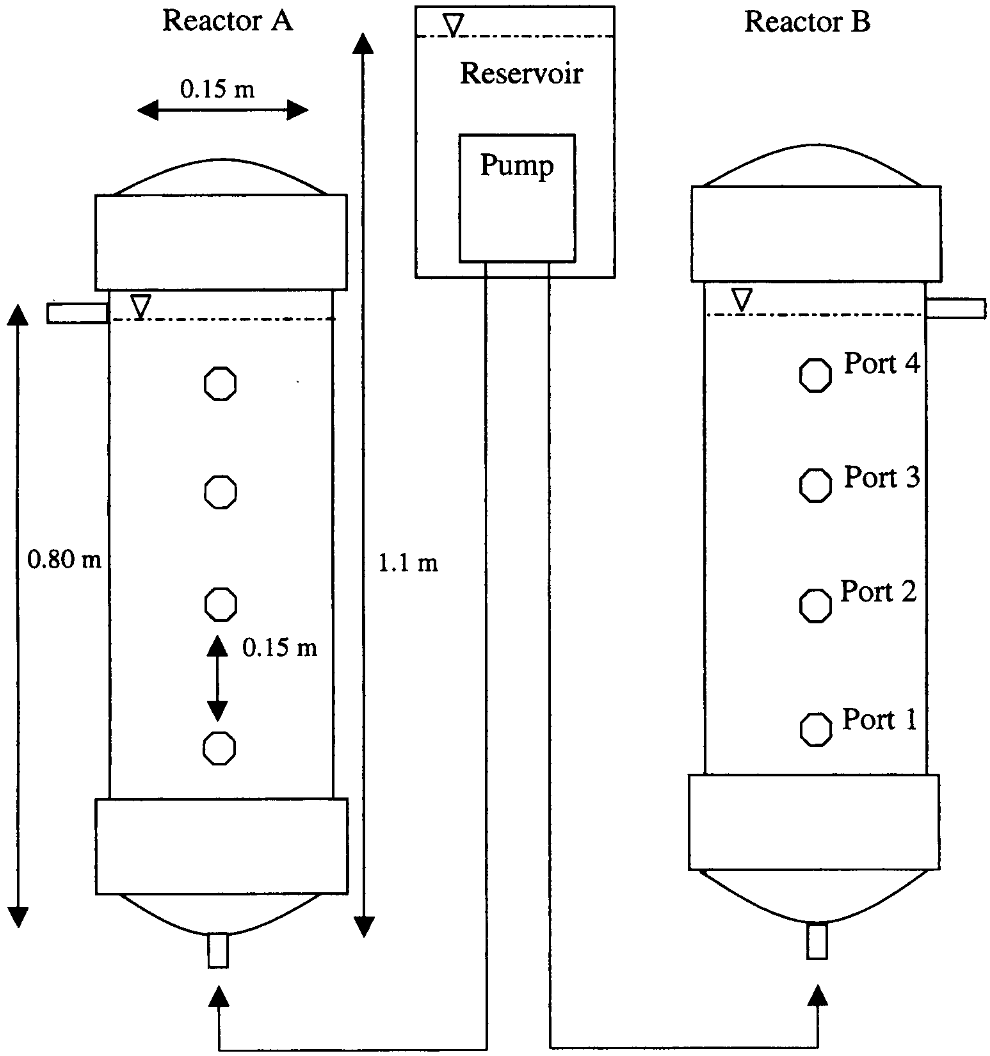


Figure 1—Schematic illustration of bench-scale reactors used for tannin removal studies.

constructed wetlands and facultative pond, although recirculation was only used at the Glen Ellen facility during the study period.

The field constructed wetlands included inlet and outlet manifolds that uniformly distributed flows across the full width at the wetland surface at the inlet as well as collected subsurface flows across the full width at the wetland bed base at the outlet. Both full-scale constructed wetlands used 1.1- to 1.2-m-thick "washed" pea (~4 mm) gravel (Glen Ellen) or rock (Hopland) substrates with established cattails and bulrush vegetation, and were designed to maintain water depths of 1.0 m. The crushed rock (10 to 30 mm) used at the Hopland constructed wetlands was not washed and was found to contain some soil and fines resulting in low, plugged-flow zones of the constructed wetlands. In addition, the Hopland constructed wetlands was not lined, but regular mass-balance measurements suggested that there was minimal, if any, seepage. The Glen Ellen constructed wetlands was lined with 1.5-mm (60-mil) polyethylene and also exhibited no seepage. The larger Hopland system (50 m wide × 88 m long) was designed for an HRT of approximately 10 days, while the Glen Ellen system (8 m wide × 38 m long) was designed for an HRT of approximately 5 days. Grids of sampling ports (16 ports at a depth of approximately 0.45 m in three evenly spaced parallel transects at the Hopland constructed wetlands and 10 dual-depth ports [approximately 0.4 and 0.95 m] in two transects at the Glen Ellen constructed wetlands) were installed to track potassium bromide tracer concentrations and water quality changes across the constructed wetlands.

Impulse-type potassium bromide tracer studies were conducted at the Hopland system in September 1999, April 2000, and October 2000 and at the Glen Ellen constructed wetlands in April 2000 to evaluate HRTs for the constructed wetlands. Because of winery expansion, the wastewater flowrate had increased by approximately 150% over design rates at the Hopland constructed wetlands, while the wastewater flowrate was less than the design rate at the Glen Ellen constructed wetlands. In the first two studies at the Hopland constructed wetlands, inflow and outflow rates were measured and samples were collected from all ports and the outlet at approximately 8- to 12-hour intervals for immediate potassium bromide analysis. In October 2000, observed fee-water conditions and apparent short-circuiting at the Hopland constructed wetlands resulted in a second test being conducted in which only outlet potassium bromide concentrations were measured at 10- to 15-minute intervals following potassium bromide injection. Tracer studies at the Glen Ellen constructed

Table 2—Average flowrates and HRTs for bench-scale experiments.

	Reactor A		Reactor B		Average	
Experiment no.	Flowrate (L/d)	HRT (d)	Flowrate (L/d)	HRT (d)	Flowrate (L/d)	HRT (d)
1	3.86	1.6	3.80	1.5	3.83	1.6
2	4.40	1.4	4.10	1.4	4.25	1.4
3	2.15	2.8	1.72	3.3	1.94	3.1

wetlands also used this more rapid sampling approach and included port sampling at two depths in repeated potassium bromide injections. The HRTs associated with the potassium bromide center of mass for each tracer study were calculated using the method-of-moments (Grismer and co-workers, 2001b) and compared with time to tracer peak (t_p) concentration and plug-flow retention times (T_d) to estimate the degree of short-circuiting, if any, in each constructed wetlands. Potassium bromide recovery during the tracer tests ranged from approximately 90 to 105% of the input mass.

Water quality samples were collected in the spring between April 18 and May 8, 2000, at both constructed wetlands and then in the fall from September 18 to October 13, 2000, at the Hopland constructed wetlands to evaluate system performance during both off-season and harvest–crush periods, respectively. The wastewater flowrate was maintained constant in both systems (e.g., approximately 137 m^3/d at the Hopland constructed wetlands) and inflow and outflow rates remained practically the same during the day, suggesting minimal evapotranspiration losses. Samples (200 mL) were analyzed daily for TDS, pH, TSS, COD, tannins, nitrate, phosphate, sulfate, sulfide, and settleable solids. Split samples (20 mL) were also acidified (2% sulfuric acid) and chilled for later TKN and ammonium analyses by the University of California, Davis, Division of Agriculture and Natural Resources Analytical Laboratory.

In the field and laboratory, chemical constituents were measured promptly using spectrophotometric methods (Hach Co., Loveland, Colorado) that are equivalent to accepted methods (APHA et al., 1998) (Table 1). Quantification of tannin concentrations is often difficult because no widely accepted test is available. While the Folin–Ciocalteau method is generally used to determine total phenolics (Ritta, 1985), tannic acid, a type of hydrolyzable tannin, is typical in winery wastewater and this spectrophotometric method was found to better measure tannic acid concentrations. Samples for TSS, tannin, phosphate, sulfate, and sulfide were diluted 1:4 for analysis purposes, while undiluted samples were analyzed for TDS, pH, COD, and nitrate. Approximately 10 to 15 samples were averaged for each port and constituent that was measured at the Hopland constructed wetlands.

In addition to the field evaluations, three bench-scale tannin (and COD) removal experiments were conducted from April to June 2001 using duplicate pea-gravel-filled cylindrical schedule 40 polyvinyl chloride reactors (150 mm diameter × 0.76 m tall) with working volumes of approximately 13.9 L (Figure 1). The reactors were shaken during filling with pea gravel to obtain packing-bulk densities similar to that found in the field, resulting in porosities of 44% for reactor A and 41% for reactor B, or pore volumes of 6.1 and 5.7 L, respectively. Upflow conditions were maintained in the reactors using a multistage peristaltic pump. Sampling ports were located at 150-mm intervals along each reactor as well as at the influent and effluent ends.

The reactors were filled with wastewater inoculum from the pilot-scale constructed wetlands (Shepherd et al., 2001a) that consisted of fermented grape juice and dextrose (1000 mg/L each) for 3 days then flushed with tap water and refilled with wastewater inoculum for another 3 days, after which synthetic wastewater was introduced at a steady rate. Synthetic wastewater containing 20 mL/L of white grape juice (tannin free) and 50 mg/L of reagent-grade tannic acid for organic loads of approximately 1000 mg COD/L was used to simulate wastewater in the full-scale constructed wetlands. The first two experiments used a steady flowrate of approximately 4 L/d (or HRTs of approximately 1.5 days) and samples were drawn twice daily (for 7 and 8 days, respectively) from all ports and analyzed for tannin and COD concentrations. The third experiment was conducted in the same manner, but used a smaller flowrate (approximately 2 L/d) to better simulate field conditions for constructed wetlands having retention times of approximately 5 days; this experiment continued for 13 days. Sample volumes of approximately 5 mL did not appreciably alter reactor volumes. Table 2 summarizes the flow conditions for the bench-scale experiments. Average reactor temperatures were 19 °C.

Tracer Study Results

Werner and Kadlec (2000) and Grismer and co-workers (2001b) underscore the need to determine the three-dimensional hydraulic performance of constructed wetlands prior to evaluation of their treatment potential so as to better determine appropriate removal models (e.g., Kadlec, 2000) as well as provide insight to remedial measures necessary to improve system performance. The tracer study results are briefly considered in this context, particularly because the treatment performance of the Hopland constructed wetlands had been compromised by excessive solids loading. Table 3 summarizes the results of the September 1999 and April 2000 tracer studies at the Hopland constructed wetlands.

Analysis of the outflow residence-time-distribution (RTD) curves from the first two tracer studies at the Hopland constructed wetlands yielded an HRT of only 133 hours (5.5 days), which was approximately one-half of that of the design HRT and less than the plug-flow retention time of 172 hours (7.2 days), suggesting some system short-circuiting as water passed through the constructed wetlands more rapidly than predicted by the system flowrate, constructed wetlands dimensions, and porosity of the wetland bed. Analysis of the RTD curves from ports within the constructed wetlands helped to identify where short-circuiting was located in the constructed wetlands for possible focused remediation as summarized in Table 3. Initially, flow was faster on the north side of the wetlands, indicating some form of short-circuiting specific to that side as verified by visual inspection of overland or preferential flows on this side. At the first set of ports, the center-line retention times matched plug-flow values, while those on the south side were actually slower than predicted, suggesting that some small flow

Table 3—Peak (t_p), observed (t_d), and plug-flow (T_d) HRTs of potassium bromide tracer at the Hopland constructed wetlands in October 1999 and 2000.

Distance from inlet	Transect	t_p (h)	t_d (h)	T_d (h)	Indications
	Outlet	85	133	172	Short-circuiting as t_p and $t_d < T_d$.
24.6 m	North	25	14	50	Greater flow on north side compared with center and south sides
	Center	25	50	50	
	South	25	51	50	
38.5 m	North	25	44	78	Flow exceeds plug-flow estimate on all three transects. Flow continues to be greater on the north side.
	Center	48	67	78	
	South	48	56	78	
53.8 m	North	108	114	109	Flow exceeds plug-flow estimate on center and south transects. Flow is less on north, indicating local area of restricted flow (fine particles).
	Center	61	96	109	
	South	61	65	109	
69.2 m	North	48	109	140	At this location, flows have increased on the south side, suggesting possible overland flow.
	Center	96	117	140	
	South	60	100	140	

restriction was present on the south side. By the second set of ports into the constructed wetlands, flow was faster than predicted by plug flow at all ports, especially on either side. Again, this could have been due to preferential flow through standing water on the sides of the constructed wetlands. However, by the third set of ports, flow was substantially slower on the north side. The third north-side port was intentionally placed in a sandy area as it was uncertain how influential the sandy areas were on flow. Water within the constructed wetlands seemed to flow around these areas, effectively reducing the size of the bed. By the final set of ports, all flow was faster than plug-flow predictions, especially on the south side. Overall, the tracer study indicated that the HRT of the constructed wetlands in the fall of 1999 and April 2000 was approximately 1.7 days less than the plug-flow HRT and that areas of limited flow existed in the constructed wetlands.

The October 2000 tracer study was initially conducted in the same manner as the previous two. However, little potassium bromide was detected in the first few 8- to 12-hour sampling periods. With the obvious surface flow conditions, a second rapid sampling impulse study was conducted. Sampling was conducted only at the outlet for the first 5 hours of the test, after which sampling occurred every hour and then less frequently as the tracer was observed to leave the system. Sampling continued at 12-hour intervals until a storm ended the study period after 4 days. The measured peak potassium bromide concentration of the outlet RTD curve from the second test occurred at 45 minutes following introduction of the tracer, and more than 75% of the tracer mass had come through the constructed wetlands within the first hour of sampling. Despite long "tailing" of the RTD, the method-of-moments suggested an HRT of approximately 1 hour. With an HRT of only 1 hour, bulk COD removal seen in the constructed wetlands (as will be discussed in a following section) was likely limited to physical processes (i.e., solids settling).

Two tracer studies in April 2000 at the Glen Ellen constructed wetlands were conducted at a flowrate greater than the wastewater design rate, allowing for a more rapid testing period. Table 4 summarizes the HRT results across the constructed wetlands at the two different sampling depths. In the first test at the shallow sampling depth, little tracer was detected in the ports along the south side, resulting in RTD curves that were virtually flat such that HRTs were not calculated for these ports. Because of the lack of detection in the south side of the constructed wetlands, it was anticipated that the system would show some short-circuiting and that the constructed wetlands bottom was slightly sloped to the north. While observed HRTs calculated for the north-side ports were more or less similar to the plug-flow HRTs, they were all somewhat less (with the exception of the first port). However, the fact that the observed HRT at the outlet was practically the same as the plug-flow HRT indicates little short-circuiting in this system as a whole. It is possible that at this mid-depth in the constructed wetlands there was some uneven gravel packing. Results from the second tracer test (at the 0.95-m depth) were similar to the first, except that practically equal tracer concentrations were found in both sides of the constructed wetlands, confirming that possible uneven packing near the surface, rather than bottom slope, was the cause of the observations in the first tracer test. Again, the observed outlet HRT was similar to the plug-flow HRT, indicating little, if any, short-circuiting across the Glen Ellen constructed wetlands.

Water Quality Results and Discussion

Monitoring of the range of water quality parameters across the Hopland constructed wetlands during the noncrush and crush periods demonstrated the variability in wastewater characteristics encountered as well as the problems associated with substantially increased short-circuiting between monitoring periods. Tables 5 and 6 summarize average variation and removal rates of the parameter concentrations across the inlet and outlet during the noncrush and crush periods, respectively. Relatively constant phosphate concentrations (approximately 1 mg/L) were not included in the tables because of their lack of variability and slight increase in concentration across the constructed wetlands. Calculated organic (COD) loading rates during the noncrush and crush periods (accounting for a small evapotranspiration concentration within the constructed wetlands [Carr, 2001]) were approximately 210 and approximately 720 kg/(ha·d), respectively. These loading rates exceeded design rates, but were comparable to those applied to the pilot-scale constructed wetlands system by Shepherd et al. (2001a).

Winery wastewater strength (COD concentration) and variability during the crush season are considerably greater than during the noncrush season. Overall COD removal rates (as well as those for most constituents listed in Tables 5 and 6) were far greater during the noncrush sampling period compared with the crush period

Table 4—Observed (t_d) and plug-flow (T_d) HRTs of potassium bromide tracer at the Glen Ellen constructed wetlands.

		0.30- to 0.45-m depth		0.95-m depth	
Distance from inlet	**Transect**	**T_d (h)**	**t_d (h)**	**T_d (h)**	**t_d (h)**
6.0 m	North	1.47	1.65	1.46	ND[a]
	South			1.46	ND
12.1 m	North	2.94	2.93	2.93	3.14
	South			2.93	3.15
18.3 m	North	4.4	4.24	4.39	4.28
	South			4.39	4.03
27.4 m	North	6.61	6.49	6.59	6.31
	South			6.59	5.84
35 m	North	8.45	7.57	8.42	8.41
	South			8.42	8.25
Outlet		8.89	8.65	8.85	8.66

[a] ND = not determined.

because of the inlet COD loading being approximately one-quarter of that during the crush period and the HRT being at least an order of magnitude greater. Figure 2 displays the COD concentration and standard deviation across the centerline length of the Hopland constructed wetlands during the noncrush and fall crush sampling periods and further illustrates the problems with short-circuiting during the crush sampling period.

Despite severe short-circuiting and solids overloading, the Hopland constructed wetlands achieved significant wastewater treatment. From a load perspective, it removed approximately 1200 kg COD/(ha·d), even with an HRT of just 1 hour. The constructed wetlands had been designed to remove a maximum of approximately 2700 kg COD/(ha·d) and 1200 kg/(ha·d) under regular operation. Clearly, more complete treatment would have occurred had the subsurface-flow conditions been restored and channeling across the constructed wetlands been reduced, as was later achieved through burning off of the vegetation and "ripping" of the rock substrate following this study.

Lack of short-circuiting and much smaller loading rates at the Glen Ellen constructed wetlands resulted in considerably different performance characteristics compared with those of the Hopland constructed wetlands. From limited grab sampling during crush and noncrush periods, the average COD and TSS concentrations to the aeration pond and from the pond to the constructed wetlands were 8000 mg COD/L and 630 mg/L and 300 mg COD/L and 175 mg/L, respectively. Average inlet and outlet COD and TSS concentrations to the constructed wetlands were only 290 mg COD/L and 145 mg/L and approximately 7 mg COD/L and 2 mg/L, respectively, yielding COD and TSS removal rates of approximately 98%. More importantly, perhaps, the outlet COD and TSS concentrations of less than 10 mg/L suggest that practically complete removal of organic loads from the winery wastewater is possible.

Removals of TSS, COD, sulfate, sulfide, tannins, and nitrate were modeled using either first-order or retarded first-order decay (i.e., Shepherd et al., 2001b) equations. Reaction rates were considered retarded when they changed along the length of the constructed wetlands. The retarded first-order decay equation developed from the simple first-order expression is given here.

$$C_t = C_o \exp[-k/R \ln(1 + Rt_d)] \tag{1}$$

Where

C_t = constituent concentration at time t (mg/L),
C_o = initial constituent concentration (mg/L),
t_d = detention (HRT) time (d),
k = reaction rate constant (1/d), and
R = retardation coefficient (1/d).

Note that when $R = 0$, eq 1 reduces to the simple first-order decay model.

Table 5—Summary of inlet and outlet water quality statistics and removal rates across the Hopland constructed wetlands during noncrush period.

	Inlet			Outlet			
Constituent (mg/L)	***n***	**Mean**	**Standard deviation**	***n***	**Mean**	**Standard deviation**	**Removal rate (%)**
TSS	15	1042	251	19	110	103	85
COD	15	1721	439	19	362	676	79
Tannin	13	55.0	16.4	18	12.1	3.8	78
Nitrate	16	1.8	0.7	18	0.5	0.5	73
Ammonium	2	118	NA[a]	4	45	11	62
TKN	2	159	NA	4	54	15	66
Sulfate	4	35	19	9	2.0	2.5	95
Sulfide	14	0.56	0.20	16	0.12	0.10	78

[a] NA = not available.

Table 6—Summary of inlet/outlet water quality statistics and removal efficiencies across the Hopland constructed wetland during crush period.

	Inlet			Outlet			
Constituent (mg/L)	*n*	Mean	Standard deviation	*n*	Mean	Standard deviation	Removal efficiency (%)
TSS	11	1428	644	13	808	229	30
COD	11	7406	2090	13	3748	1826	49
Tannin	10	55.2	21.6	12	30.0	20.6	46
Nitrate	7	13.1	7.4	8	10.9	4.3	17
Ammonium	5	37	28	5	26	5	29
TKN	5	43	31	5	32	6	25
Sulfate	8	83	33.5	8	62	39	25
Sulfide	11	0.88	0.5	13	0.7	0.2	20

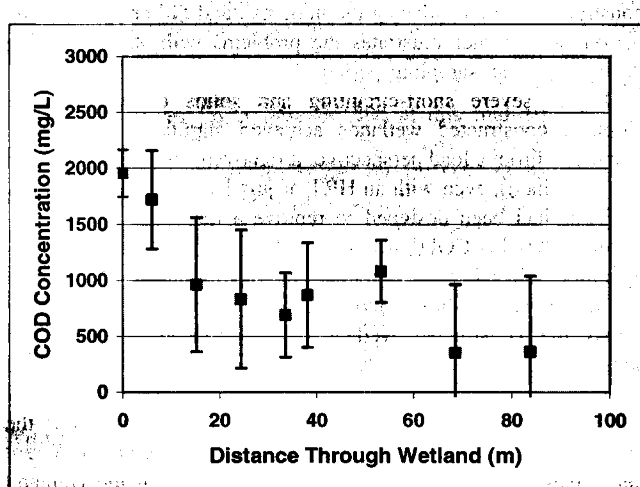
For example, the retarded first-order decay model was applied to TSS removal because of the differential removal of particles resulting from flocculation, straining, and settling along the constructed wetlands. As larger particles preferentially settle first, the TSS removal rate depends on the detention time, or distance through the constructed wetlands. Sulfide and nitrate removal also seemed to be better modeled by the first-order retarded degradation equation. Table 7 summarizes model coefficients determined from the best least-squares fitting of both equations to the measured concentrations as they varied with distance along the Hopland constructed wetlands, assuming a t_d of 5.5 days. Modeling of TKN and ammonia degradation was unsuccessful because of insufficient data at short detention times and, therefore, is not included. Sulfide and nitrate concentrations were at trace levels (concentrations ranging from 0 to 2 mg/L), resulting in relatively large standard deviations, poor model fitting, and ambiguous decay and retardation coefficients. Because the HRT of the Hopland constructed wetlands during the crush season was compromised by excessive short-circuiting, no attempts were made to model results from this period.

Tannin Removal: Results and Discussion

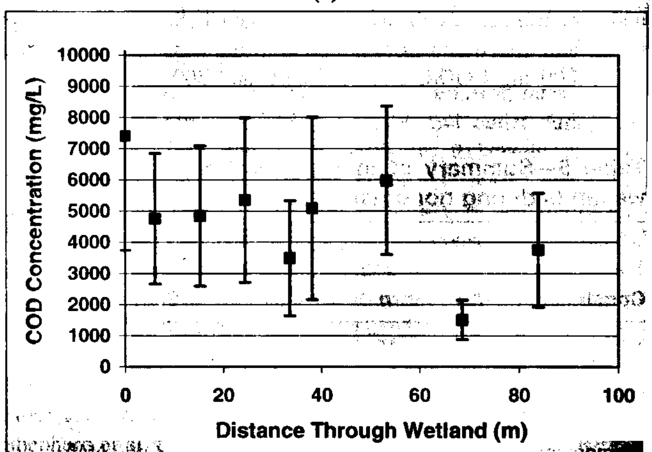
Average wastewater removal efficiency changed unexpectedly between periods when the three bench-scale reactor experiments were conducted, although the two reactors behaved nearly identically in each experiment. Despite doubling the HRT between the first two experiments and the third, both COD and tannin removal decreased (Table 8). It seems that either a steady-state condition was not reached or there was sloughing of organic material within the reactors between experiments.

Figure 3 illustrates average tannin removal within the reactors and the first-order decay (plug-flow) model coefficients for each experiment (Crites and Tchoblanoglous, 1998). Tannin decay coefficients and relative model fit (R^2 value) decreased with increasing HRT. However, overall tannin removal rates were approximately the same for the first and third experiments (Table 8), suggesting that these coefficients may have limited meaning such that an intermediate value may be appropriate. In each of the curves shown in Figure 3, tannic acid concentration initially decreases more rapidly than predicted by the first-order model and then levels off, suggesting that the reactors were of sufficient length to reach an approximate steady-state condition with respect to tannin degradation along the column length. This effect may also be attributed to differential ripening in the reactor or concentration of organic matter near the reactor inlet, a common "plugging" problem with sand and gravel filters.

Tannin concentrations and removal rates in the Hopland constructed wetlands were quite similar to those in the bench-scale reactors during both noncrush and crush periods at the winery (Tables 5 and 6). Average inlet tannin concentrations were approximately 55 mg/L during both periods, while average outlet concentrations ranged from 12 to 30 mg/L for removal efficiencies



(a)



(b)

Figure 2—Concentration and variance of COD with distance along the Hopland constructed wetland center line: (a) spring noncrush period and (b) fall crush period

Table 7—First-order decay constants and retardation coefficients for constituent removal in the Hopland constructed wetlands during the noncrush season.

Constituent	k (d^{-1})	R (d^{-1})	R^2[a]
COD	0.31	0	0.78
Tannin	0.29	0	0.78
Sulfate	0.54	0	0.89
TSS	0.41	0.2	0.78
Sulfide	0.28	0.2	0.57
Nitrate	0.24	0.5	0.59

[a] Least-squares analysis.

of 78 to 48%, respectively, values similar to those found in the literature. Decreased tannin removal during the fall crush period was not surprising because of the extremely short effective HRT and high COD loads.

Figure 4 illustrates the variability of tannin degradation across the Hopland constructed wetlands during the noncrush and crush periods. Replacing distance along the constructed wetlands with the average HRT of 5.5 days for all three transects across the constructed wetland results in an average first-order decay coefficient of approximately 0.3 d^{-1} (R^2 = 0.77) that is similar to the value from the bench-scale data. During the crush period (Figure 4b), however, the tannin decay coefficient determined using an HRT of 1 hour is far greater (approximately 17 d^{-1} and R^2 = 0.49); an HRT of 1 day yields a more reasonable coefficient of approximately 0.7 d^{-1}. Tannin degradation in either system does not seem to be as recalcitrant as anticipated from the literature; rather, removal rates of 50 to 80% can be expected in these systems.

Summary and Conclusions

Use of constructed wetlands for winery wastewater treatment has the advantages associated with low operating costs and the ability to effectively assimilate the variably high organic loadings characteristic of winery wastewater production. Lignins, tannins, and other polyphenolics common in winery wastewater also pose particular treatment concerns because of potential downstream effects on aquatic life. However, little is known about the effectiveness of winery wastewater treatment by constructed wetlands in the field as the literature lacks evaluations of full-scale winery wastewater treatment systems.

Table 8—Chemical oxygen demand and tannin removal rates for bench-scale reactor experiments.

Experiment	Average inlet concentration (mg/L)	Average outlet concentration (mg/L) Reactor A	Reactor B	Average removal (%)
COD				
1	1247	347	348	72
2	1094	364	387	66
3	887	366	366	59
Tannin				
1	52.5	22.3	22.2	58
2	47.7	28.4	30.3	38
3	50.2	22.6	23.4	54

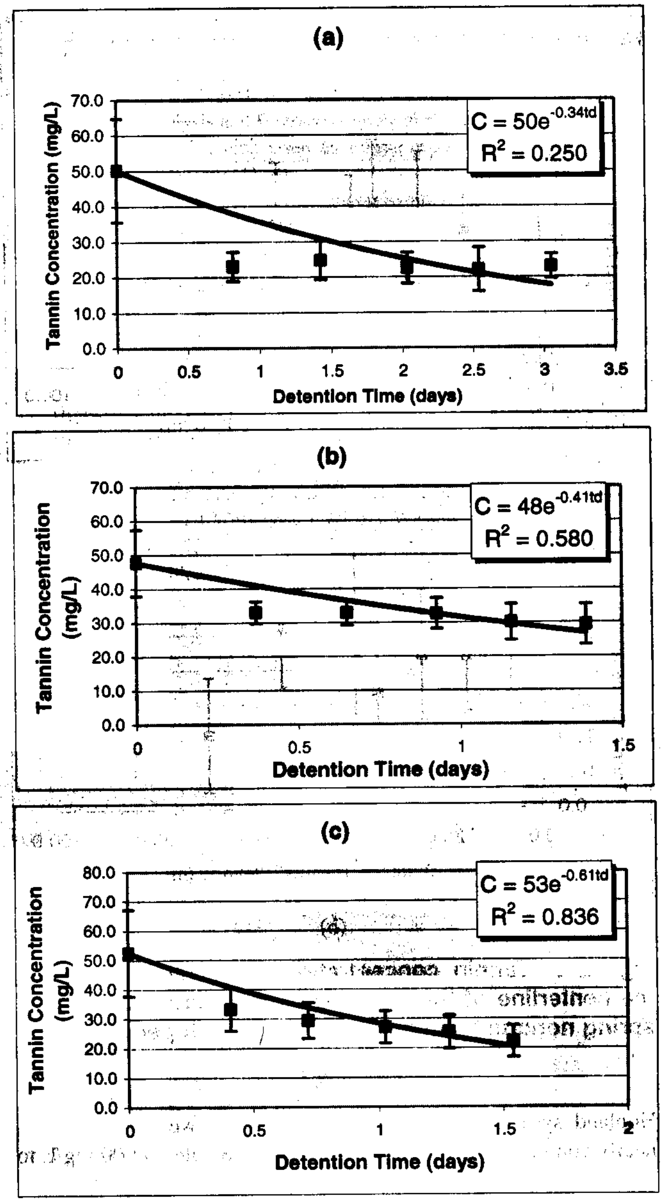


Figure 3—Averaged tannin removal from both reactors, its variability, and modeled decay: (a) experiment 3, (b) experiment 2, and (c) experiment 1.

Bench- and full-scale evaluations were conducted during 2000 and 2001 to quantify treatment efficiencies and model constituent degradation in constructed wetlands for winery wastewater treatment. Results were quite variable in the full-scale system, especially during the harvest–crush fall season. Chemical oxygen demand removal rates ranged from 59 to 72% for the simple bench-scale reactors, while tannin removal ranged from 54 to 58%. The Hopland constructed wetlands showed similar COD and tannin removal rates ranging from 49 to 79% and 46 to 78%, respectively, with greater removal occurring during the spring noncrush period. Although at smaller loading rates and greater HRTs than in the

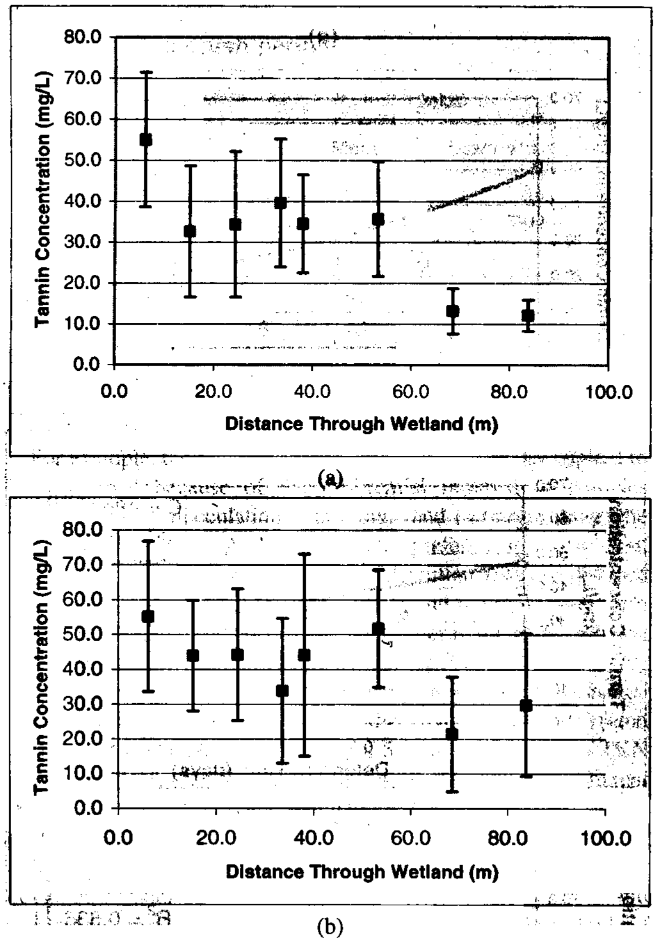


Figure 4—Tannin concentrations and variations along the centerline of the Hopland constructed wetlands: (a) spring noncrush period and (b) fall crush period.

Hopland system, the Glen Ellen constructed wetlands achieved nearly complete COD removal (from approximately 8000 mg/L to 5 mg/L) through use of the recirculation system, suggesting that, when properly loaded and operated, the system was quite capable of full treatment of winery wastewater.

First-order degradation models were applied for bench-scale tannin removal, and both first-order and retarded first-order decay equations were used to model full-scale constituent degradation. Although wastewater COD strength was much greater for the full-scale constructed wetlands, tannin loading and removal were similar in both the laboratory and field studies. Despite the shorter HRTs in the bench-scale reactors, tannin decay-rate constants for both systems were similar (approximately 0.3 d^{-1}). Determination of winery wastewater tannin composition during crush and noncrush periods as well as supplemental photodegradation of tannins in constructed wetlands may be a promising area for research.

Because of short-circuiting in the Hopland constructed wetlands prior to crush-season measurements, it was difficult to quantify actual treatment potential of this constructed wetlands. Although removal rates were substantially greater during the spring, it was not clear whether similar efficiencies could be obtained during the crush season had the constructed wetlands not been compromised. Nonetheless, despite HRTs on the order of 1 hour during the crush season compared with approximately 5 days during the noncrush season, the constructed wetlands reduced inlet COD by one-half while reducing other constituents by 20 to 30%. Understanding the HRTs of the constructed wetlands through tracer study analyses was crucial to interpretation of the water quality measurements across the constructed wetlands.

Acknowledgments

Authors. M. E. Grismer is a professor of Hydrology and Biological & Agricultural Engineering at the University of California, Davis; M. A. Carr is a former graduate student in Biological & Agricultural Engineering at the University of California, Davis; and H. L. Shepherd is an environmental engineer–scientist with Komex-H20 Science, Huntington Beach, California. Correspondence should be addressed to M. E. Grismer, 1 Shields Avenue, LAWR–Hydrology, UC Davis, Davis, California, 95616; e-mail: megrismer@ucdavis.edu.

Submitted for publication January 28, 2002; revised manuscript submitted October 21, 2002; accepted for publication October 29, 2002.

The deadline to submit Discussions of this paper is January 15, 2004.

References

American Public Health Association; American Water Works Association; Water Environment Federation (1998) *Standard Methods for the Examination of Water and Wastewater*, 20th ed.; Washington, D.C.

Bhat, T. K.; Singh, B.; Sharma, O. P. (1998) Microbial Degradation of Tannins—A Current Perspective. *Biodegradation*, **9** (5), 343.

Biosystems, Inc. (1993) *Lower Moukolemne River Management Plan*; Vol. 3, 1990–1992; San Francisco, California.

Carr, M. A. (2001) The Use of Constructed Wetlands to Treat Winery Wastewater. M.S. Thesis, *Biological and Agricultural Engineering*, University of California, Davis.

Crites, R.; Tchoblanoglous, G. (1998) *Small and Decentralized Wastewater Management Systems;* WCB/McGraw-Hill: Boston, Massachusetts.

Cronin, C.; Lo, K. V. (1998) Anaerobic Treatment of Brewery Wastewater Using UASB Reactors Seeded with Activated Sludge. *Bioresour. Technol.*, **64** (1), 33.

Etnier, C.; Guterstam, B., Eds. (1997) *Ecological Engineering for Wastewater Treatment*, 2nd ed.; Proceedings of the Conference at Stensund Folk College, Sweden, March 24–28; Lewis Publishers: Boca Raton, Florida.

Grismer, M. E.; Carr, M. A.; Shepherd, H. L. (1999) Fermentation Industry. *Water Environ. Research*, **71**, 805.

Grismer, M. E.; Carr, M. A.; Shepherd, H. L. (2000) Fermentation Industry. *Water Environ. Research*, **72** (5), Literature Review [CD-ROM].

Grismer, M. E.; Ross, C. C.; Valentine, G. E.; Smith, B. M.; Walsh, J. L. (2001a) Literature Review: Food Processing Wastes. *Water Environ. Res.*, **73** (5), Literature Review [CD-ROM].

Grismer, M. E.; Shepherd, H. L. (1998) Fermentation Industry. *Water Environ. Res.*, **70**, 637.

Grismer, M. E.; Tausendschoen, M.; Shepherd, H. L. (2001b) Subsurface Flow Hydraulic Characteristics of a Constructed Wetland for Treatment of Winery Effluent. *Water Environ. Res.*, **73**, 466.

Jewell, W. T.; Ebeler, S. E. (2001) Tyrosinase Biosensor for the Measurement of Wine Polyphenolics. *Am. J. Enol. Viticulture*, **52** (3), 219.

Kadlec, R. H. (2000) The Inadequacy of First-Order Treatment Wetland Models. *Ecol. Eng.*, **15**, 105.

Kalyuzhnyi, S. V.; Gladchenko, M. A.; Sklyar, V. I.; Kizimenko, Y. S.; Shcherbakov, S. S. (2001a) Psychrophilic One- and Two-Step Systems for Pre-Treatment of Winery Waste Water. *Water Sci. Technol.*, **44** (4), 23.

Kalyuzhnyi, S. V.; Gladchenko, M. A.; Sklyar, V. I.; Kizimenko, Y. S.; Shcherbakov, S. S. (2001b) One- and Two-Stage Upflow Anaerobic Sludge-Bed Reactor Pretreatment of Winery Wastewater at 4–10 C. *Appl. Biochem. Biotechnol.*, **90**, 107.

Kalyuzhnyi, S. V.; Gladchenko, M. A.; Sklyar, V. I.; Kurakova, O. V.; Shcherbakov, S. S. (2000) The UASB Treatment of Winery Wastewater under Submesophilic and Psychrophilic Conditions. *Environ. Technol.*, **21**, 919.

Larson, C. (1999) Constructed Wetlands Research Offers Treatment for Wastewater: Fetzer, Benziger Wineries Pioneer 'Green' Systems. *Wine Business Monthly*, **6** (12), 43.

Laubscher, A. C. J.; Wentzel, M. C.; Le Roux, J. M. W.; Ekama, G. A. (2001) Treatment of Grain Distillation Wastewaters in an Upflow Anaerobic Sludge Bed (UASB) System. *Water SA (Pretoria)*, **27**, 433.

Petroccioli, M.; Duarte, J. C.; Federici, F. (2000) High-Rate Aerobic Treatment of Winery Wastewater Using Bioreactors with Free and Immobilized Activated Sludge. *J. Biosci. Bioeng.*, **90**, 381.

Ritta, J.-T. (1985) Phenolic Constituents in the Leaves of Northern Willows: Methods for the Analysis of Certain Phenolics. *J. Agric. Food Chem.*, **33**, 213.

Ronquest, L. C.; Britz, T. J. (1999) Influence of Lower pH and Retention Time on the Efficiency of a UASB Bioreactor Treating Winery Wastewater. *South African J. Enol. Viticulture*, **20** (1), 35.

Sarni-Manchado, P.; Deleris, A.; Avallone, S.; Cheynier, V.; Moutounet, M. (1999) Analysis and Characterization of Wine Condensed Tannins Precipitated by Proteins Used as Fining Agent in Enology. *Am. J. Enol. Viticulture*, **50** (1), 81.

Shepherd, H. L. (1998) Performance Evaluation of a Pilot-Scale Constructed Wetland Used for Treatment of Winery Process Wastewater. *Second International Specialized Conference on Winery Wastewaters*, Bordeaux, France, May 5–7; INRA and Camagraf: France; pp 155–163.

Shepherd, H. L.; Grismer, M. E. (1997) Constructed Wetlands for Wastewater Disposal. *Vineyard Winery Manage.*, **23** (5), 65.

Shepherd, H. L.; Grismer, M. E.; Tchobanoglous, G. (2001a) Treatment of High-Strength Winery Wastewater Using a Subsurface Flow Constructed Wetland. *Water Environ. Res.*, **73**, 394.

Shepherd, H. L.; Tchobanoglous, G.; Grismer, M. E. (2001b) Time-Dependent Retardation Model for COD Removal in a Subsurface Flow Constructed Wetland for Winery Wastewater Treatment. *Water Environ. Res.*, **73**, 567.

Werner, T. M.; Kadlec, R. H. (2000) Wetland Residence Time Distribution Modeling. *Ecol. Eng.*, **15**, 77.