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Using Constructed Wetlands to Treat Biochemical Oxygen Demand and Ammonia Associated with a Refinery Effluent

George M. Huddleston,*[,1] W. Barry Gillespie,† and John H. Rodgers*

**Clemson Institute of Environmental Toxicology, Clemson University, 509 Westinghouse Road, Pendleton, South Carolina 29670; and*
†ENTRIX, Inc., 5252 Westchester, Suite 250, Houston, Texas 77005

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This study evaluated the effectiveness of constructed wetlands for tertiary treatment of a petroleum refinery effluent. Specific performance objectives were to decrease 5-day biochemical oxygen demand (BOD_5) and ammonia by at least 50% and to reduce toxicity associated with this effluent. Two bench-scale wetlands (replicates) were constructed in a greenhouse to provide tertiary treatment of effluent samples shipped from the refinery to the study site. Integrated wetland features included *Typha latifolia* Linnaeus planted in low organic (0.2%), sandy sediment, 48-h nominal hydraulic retention time, and 15-cm overlying water depth. Targeted constituents and aqueous toxicity were monitored in wetland inflows and outflows for 3 months. Following a 2 to 3-week stabilization period, effective and consistent removal of BOD_5 and ammonia (as NH_3–N) from the effluent was observed. Average BOD_5 removal was 80%, while NH_3–N decreased by an average of 95%. Survival of *Pimephales promelas* Rafinesque and *Ceriodaphnia dubia* Richard (7-day, static, renewal exposures) increased by more than 50% and 20%, respectively. Reproduction of *C. dubia* increased from zero in undiluted wetland inflow to 50% of controls in undiluted wetland outflow. This study demonstrated the potential for constructed wetlands to decrease BOD_5, ammonia, and toxicity in this refinery effluent. © 2000 Academic Press

Key Words: **constructed wetlands; biochemical oxygen demand; ammonia; refinery effluent; toxicity.**

INTRODUCTION

Among the constituents of petroleum refinery effluents often targeted for remediation are 5-day biochemical oxygen demand (BOD_5) and ammonia. Both parameters are regulated under the National Pollutant Discharge Elimination System (NPDES) for the petroleum industry. Therefore, effective, cost-efficient measures for decreasing concentrations of these and other constituents of discharge waters are often sought. One alternative for achieving permit compliance is through tertiary effluent treatment using constructed wetlands. Constructed wetlands are less expensive to maintain than conventional treatment methods, and they are effective for decreasing BOD and ammonia concentrations ($>50\%$ removal) in final effluents (Watson *et al.*, 1989).

Treatment of effluents containing BOD and ammonia using constructed wetlands is accomplished through several physical, chemical, and biological processes. Removal of BOD_5 in wetlands is primarily by aerobic microbial degradation and sedimentation/filtration processes (Watson *et al.*, 1989). A significant portion of oxygen needed to support aerobic degradation processes in wetlands is obtained through lacunal translocation from the atmosphere to the rhizosphere by rooted aquatic macrophytes (Reddy *et al.*, 1989; Brix, 1993; Moorhead and Reddy, 1990). Ammonia is removed from water primarily by oxidation to nitrate by nitrifying bacteria (i.e., nitrification) in aerobic wetland zones. However, this process in turn exerts an oxygen demand and contributes to the overall BOD in the system. Following nitrification, nitrate undergoes denitrification to N_2 gas in anaerobic zones (Gersberg *et al.*, 1983; Reddy *et al.*, 1989). Plant uptake and volatilization are also important mechanisms for ammonia removal (Watson *et al.*, 1989; Brix, 1993). Often overlooked is chemical oxidation of ammonia in aerobic waters. This research was conducted to evaluate the effectiveness of constructed wetlands for decreasing BOD_5 and ammonia concentrations and reducing toxicity associated with a petroleum refinery effluent.

MATERIALS AND METHODS

Integrated Design and Wetland Parameters

The overall objective of this study was to evaluate the effectiveness of constructed wetlands for tertiary treatment of effluent from a petroleum refinery. Parameters measured included BOD_5, ammonia, and toxicity. To evaluate wetland performance, two bench-scale treatment wetlands (replicates) were designed and constructed by integrating specific macrofeatures (i.e., hydrosoil, vegetation, and

[1]To whom correspondence should be addressed. Fax: 864.646.2260. E-mail: jrodger@clemson.edu.

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hydroperiod) for encouraging the transfers and transformations of targeted constituents. Integrated design involved selection of wetland macrofeatures to enhance the potential for desired chemical fate processes. The fundamental principle supporting this research was that certain desired reactions that resulted in transfers and transformations of targeted constituents (i.e., BOD and ammonia) in the aqueous matrix would be not only thermodynamically possible, but also likely if wetland macrofeatures were combined appropriately. This study was conducted in a greenhouse at the University of Mississippi Field Station, Lafayette County, Mississippi, from May to September 1997.

Hydrosoil selection. Considerations for hydrosoil selection included (1) compatibility with selected vegetation, (2) limited nutrient availability to promote plant uptake of nitrogen (in the forms of ammonium and nitrate), and (3) low organic carbon content and sufficient porosity for promoting an oxygenated rhizosphere for supporting aerobic bacteria responsible for BOD degradation and nitrification. The hydrosoil selected in this study was 75% sand, 20% silt, and $< 5\%$ clay with minimal organic carbon (0.2%) (Suedel and Rodgers, 1991).

Vegetation selection. Selected vegetation was *Typha latifolia* Linnaeus (common cattail). From a perspective of remediation of the targeted effluent constituents, this emergent macrophyte actively aerates its root zone, which could enhance microbial activity responsible for BOD degradation and oxidation of ammonia. Growth rate of *T. latifolia* is relatively rapid and decay of detritus is relatively slow ($t_{1/2} \approx 6$ mo), thus having minimal influence on BOD due to decomposition (Rodgers *et al.*, 1983).

Hydroperiod selection. Based upon discharge rates and available space at the refinery, a 48-h hydraulic retention time (HRT) was selected for the bench-scale study. Water depth associated with this HRT was maintained at 15 cm.

Bench-scale wetland specifications. Bench-scale wetlands were constructed in plastic tubs measuring 48 cm in diameter by 41 cm in height (Fig. 1). Hydrosoil volume in wetland containers was 40,000 cm^3, with a constant water volume of 23 L. Overlying water depth was maintained by an outlet port positioned 15 cm above the hydrosoil surface. Inflow rates to the bench-scale wetlands were controlled by Fluid Metering, Inc. (FMI), piston pumps, which supplied approximately 8 ml/min to achieve nominal 48-h HRTs. *T. latifolia* density increased from approximately 66 to 200 shoots/m^2 over the duration of the study (15 weeks).

Evaluation of Bench-scale Wetland Performance

Two 208-L drums of treated effluent from the refinery were shipped weekly to the study site. Aqueous samples of wetland inflows (directly from drums) and wetland outflows were collected determination of NH_3–N, BOD_5, and toxicity. Ammonia–nitrogen and BOD_5 were measured according to *Standard Methods for the Examination of Water and Wastewater* (American Public Health Association *et al.*, 1995). Toxicity was measured using *Ceriodaphnia dubia* and *Pimephales promelas* 7-day, static, renewal exposures (Peltier and Weber, 1985; Weber and Peltier, 1989; American Public Health Association *et al.*, 1995). Survival was monitored for both organisms, and reproduction was

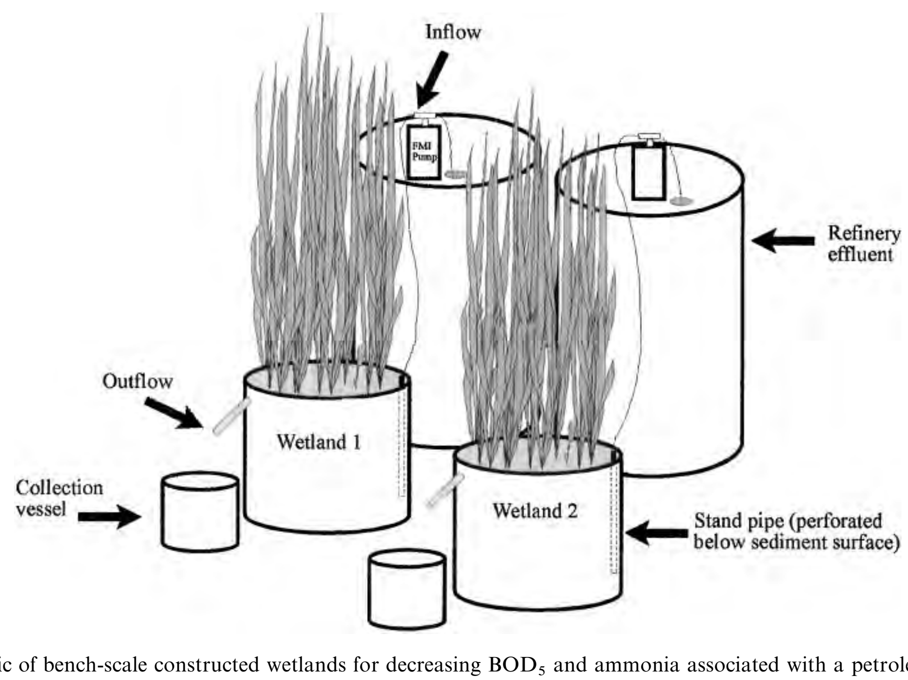

FIG. 1. Schematic of bench-scale constructed wetlands for decreasing BOD_5 and ammonia associated with a petroleum refinery effluent.

measured for *C. dubia*. Toxicity parameters (lethal concentrations and reproductive effects concentrations) were determined using a 50% dilution series ranging from 100% effluent (undiluted) to 6.25% effluent. Dilutions were prepared using filtered (0.45 μm), hardness/alkalinity adjusted (80–100 mg/L as $CaCO_3$) spring water. This source also served as control water for toxicity testing.

To evaluate constructed wetland performance, NH_3-N and BOD_5 concentrations and toxicity were measured in wetland inflows (prior to treatment) relative to wetland outflows (after treatment). Both changes in concentrations of targeted constituents (% removal) and toxicity reduction were considered in this analysis.

Statistical Evaluation of Toxicity Responses

Median lethal concentrations (LC_{50}) were calculated using Trimmed Spearman–Karber (Hamilton *et al.*, 1977). Lowest-observed effect concentrations (LOEC), as represented by reproductive impairment of *C. dubia*, were determined by Dunnett's Test or Steel's Many-One Rank Test. Tests for normality and homogeneity of variance were performed using the Shapiro–Wilk's Test and the Bartlett's Test, respectively. Calculations were performed using Tox-Calc computer software (Tidepool Scientific, 1992/93).

RESULTS

BOD_5 Removal

To facilitate data analysis and presentation of results, replicate wetlands were designated Wetland 1 and 2. All outflow values reported in this section represent concentrations or percentage removal following a 48-h HRT. After an initial period of wetland stabilization (2–3 weeks), BOD_5 of the refinery effluent was consistently abated by bench-scale constructed wetlands. Average inflow BOD_5 of Wetland 1 was 14 mg/L (range: 3–25 mg/L), and average outflow was 2 mg/L (range: <1–4 mg/L) (Fig. 2a). Overall BOD_5

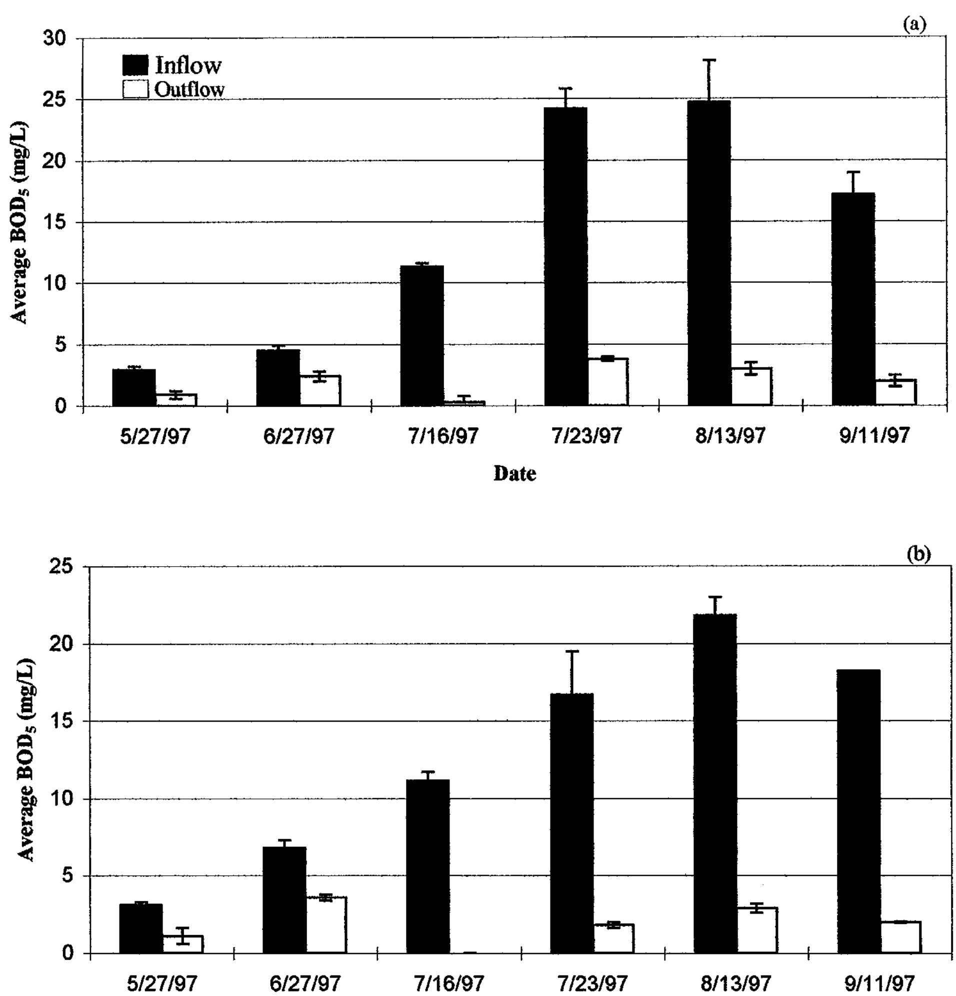

FIG. 2. Mean BOD_5 concentrations in inflows and outflows of bench-scale Wetland 1 (a) and Wetland 2 (b) receiving a petroleum refinery effluent.

removal for Wetland 1 averaged 79%. In Wetland 2, average inflow BOD_5 was 13 mg/L (range: 3–22 mg/L), and outflow BOD_5 averaged 2 mg/L (range: <1–4 mg/L) (Fig. 2b). Similarly, overall BOD_5 removal for Wetland 2 averaged 80%.

Ammonia Removal

Ammonia concentrations also significantly and consistently decreased in refinery effluent following constructed wetland treatment (Fig. 3). In Wetland 1, average inflow NH_3–N concentration was 4.16 mg/L (range: 2.18–8.4 mg/L), and average outflow concentration was 0.25 mg/L (range: 0.04–1.02 mg/L), resulting in an average removal 94%. Average inflow NH_3–N concentration in Wetland 2 was 4.53 mg/L (range: 2.15–8.6 mg/L), and average outflow concentration was 0.23 mg/L (range: 0.03–1.07 mg/L), an average removal rate of 95%.

Toxicity Reduction

Four survival tests were conducted using *P. promelas*, and three survival/reproduction tests were conducted with *C. dubia*. Duration of all toxicity experiments was 7 days. Increases in both survival and reproduction of test organisms were observed following wetland treatment. Seven-day median lethal concentrations (LC_{50}), expressed as percentage effluent, for *P. promelas* averaged 40% (± 6) for both wetland inflows (Table 1). Outflow LC_{50}s were not attainable, since $\geq 50\%$ mortality was not observed in outflow exposure concentrations. Percentage survival of *P. promelas* increased from 3% in inflow to 53% in outflow of Wetland 1. Similarly, survival in Wetland 2 increased from 1 to 62%, resulting in an overall increase in survival of more than 50% following wetland treatment. Survival of control oganisms ranged from 80 to 94% for all 7-day *P. promelas* toxicity experiments.

Ceriodaphnia dubia was less sensitive than *P. promelas* to the refinery effluent in this study. Calcultion of median lethal concentrations for *C. dubia* was not possible for inflows or outflows in the three experiments, since survival was in excess of 50%. Survival of *C. dubia* increased from 60 to 90% from inflow to outflow of Wetland 1, and from 60 to 80% from inflow to outflow of Wetland 2 (Table 1). Overall increase in survival of *C. dubia* was 20–30% after wetland treatment. Survival of control organisms ranged from 87 to 100% for all 7-day *C. dubia* toxicity experiments.

The LOECs for *C. dubia*, expressed as percentage effluent causing reproductive impairment, were 12.5% for inflow and 100% for outflow of Wetland 1, and 6.25 and 50%, respectively, for Wetland 2 (Table 1). Mean fecundity of control oganisms ranged from 10 to 17 neonates per female for all 7-day *C. dubia* toxicity experiments.

DISCUSSION

The integrated constructed wetland design evaluated in this study effectively decreased BOD_5 and ammonia associated with this petroleum refinery effluent by more than 80%. The biogeochemical processes inherent in wetland

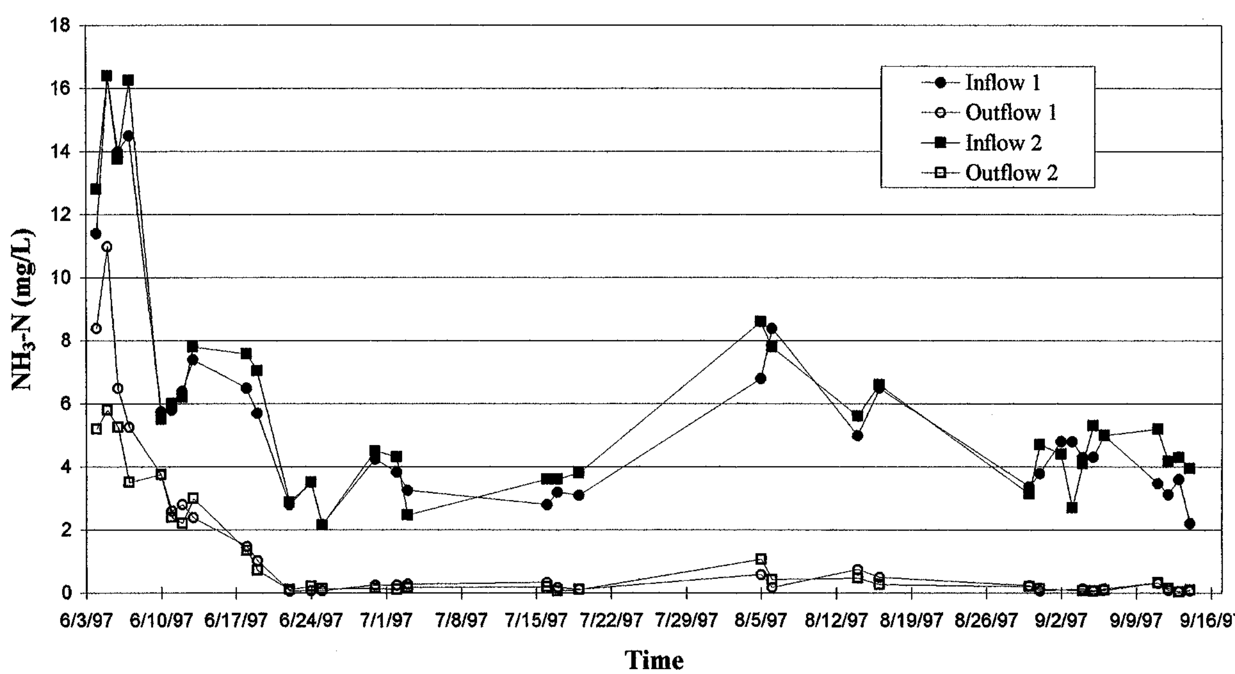

FIG. 3. Ammonia concentrations in inflows and outflows of two bench-scale constructed wetlands receiving a petroleum refinery effluent.

TABLE 1
Toxicity Data for *Pimephales promelas* and *Ceriodaphnia dubia* Exposed to a Petroleum Refinery Effluent (7-Day, Static Renewal) Prior to and Following Bench-Scale Constructed Wetland Treatment

	LC_{50}		% Survival			LOEC	
	Inflow	Outflow	Inflow	Outflow	Control	Inflow	Outflow
Wetland 1							
P. promelas	40 ($\pm$ 6)	*	3	53	89	**	**
C. dubia	*	*	60	90	93	12.5	100
Wetland 2							
P. promelas	40 ($\pm$ 6)	*	1	62	89	**	**
C. dubia	*	*	60	80	96	6.25	50

Note. LC_{50} and LOEC expressed as percentage effluent.
* Value could not be calculated due to insufficient toxicity.
** LOEC values calculated for *C. dubia* only.

systems that function to transfer and transform these effluent constituents are relatively well-understood (Mitsch and Gosselink, 1993; Manahan, 1994).

The pathway largely responsible for BOD removal in wetland hydrosoils is oxidation of the organic matter, which provides energy for microbial metabolic processes and can be synthesized or incorporated into cell mass (Manahan, 1994). The organic matter present in effluents provides a substrate for aerobic microbial metabolism. The impetus, therefore, of constructed wetlands is to encourage contact of microorganisms with this substrate, resulting in conversion of organic matter to CO_2, biomass, and water (Portier and Palmer, 1989). Thus, the design rationale for this system was that by utilizing a *T. latifolia*/sandy hydrosoil combination to encourage an oxygen-rich rhizosphere, aerobic microbial degradation of BOD would be enhanced.

The fate of ammonia in this particular wetland design likely included microbial nitrification/denitrification, volatilization, and uptake by plants (in the form of NH_4^+ or NO_3). In water, ammonia is readily reduced to ammonium or oxidized to NO_2 and NO_3. Key to the conversion of ammonium in wetland systems is nitrification, the microbially mediated process by which ammonium–nitrogen is oxidized to nitrite– and finally nitrate–nitrogen under aerobic conditions. Nitrification typically takes place in the oxidized layer of the hydrosoil surface. However, if oxygenation of the rhizosphere is sufficient, macrophyte roots also contribute to the conversion of ammonium (Good and Patrick, 1987; Reddy and Graetz, 1988). As noted above, this was the rationale behind using *T. latifolia*, a macrophyte that readily translocates oxygen to its root zone (Michaud and Richardson, 1989), and a sandy hydrosoil, providing sufficient porosity to promote an oxidized rhizosphere and support aerobic nitrifying bacteria.

Concomitant with abatement of BOD_5 and ammonia in this refinery effluent was a decrease in toxicity to *P. promelas* and *C. dubia*. Inflow NH_3-N concentrations (2–8 mg/L) measured in this study were well in excess of those known to elicit adverse effects in aquatic organisms. Several authors have reported 48-h LC_{50} values for *P. promelas* exposed to ammonia ranging from 0.73 to 3.4 mg/L (USEPA, 1985). Ammonia concentrations in outflow samples from the bench-scale wetlands ranged from 0.03 to 1.07 mg/L. Although these concentrations represented a 95% removal of influent ammonia, concentrations at the upper end of this range may have contributed to *P. promelas* toxicity. Further, *P.* promelas was more sensitive to effluent exposure than *C. dubia* in this study, providing further evidence of ammonia-induced toxicity (USEPA, 1985). Toxicity observed in this study may also be attributed to unidentified effluent constituents not targeted for remediation.

CONCLUSIONS

In this evaluation of itegratively designed, bench-scale constructed wetlands for tertiary treatment of a petroleum refinery effluent, average BOD_5 removal was 80%, while NH_3-N was decreased by an average of 95% with a 48-h wetland HRT. Toxicity was also decreased by wetland treatment, with survival of *P. promelas* and *C. dubia* (7-day, static, renewal exposures) increasing by more than 50 and 20%, respectively. Reproduction of *C. dubia* increased from zero in undiluted wetland inflow to within 50% of controls in undiluted wetland outflow. The integrated wetland design emphasizing specific wetland macrofeatures (hydrosoil, vegetation, and hydroperiod) evaluated in this study effectively decreased concentrations of the targeted effluent constituents. Implementation of these macrofeatures in a full-scale constructed wetland for tertiary effluent treatment could strongly enhance removal of BOD_5 and ammonia from this refinery effluent and enable this facility to meet NPDES permit limits for these constituents.

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