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TRANSFORMATIONS IN DISSOLVED ORGANIC CARBON THROUGH CONSTRUCTED WETLANDS

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Abstract—Constructed wetlands have emerged as a viable option for addressing a wide range of water quality problems, especially in treating wastewater effluent. This paper presents longitudinal profiles in dissolved organic carbon (DOC) concentrations and structural characteristics across a full-scale wastewater treatment wetland receiving lagoon-treated wastewater (DOC = 15–25 mg/L). DOC removal through the wetland varied seasonally, achieving a maximum net removal of 47% in February and minimum net removal of 9% in June. During summer months, when the wetland plants were actively growing, DOC decreased across the first half of the wetland and then increased through the second half of the wetland. Specific ultraviolet absorbance at 254 nm always increased across the wetland, with the largest increases (>130%) occurring during summer months. DOC lability decreased across the wetland. DOC reactivity to form trihalomethanes was also reduced on both an absolute and per carbon mass basis. Laboratory experiments employing a series of wetland microcosms with HRTs ranging from 1.6 to 7.4 days were employed to determine the amount of DOC leached from *Typha* wetland plant material. During fifty-six day steady-state experiments, roughly 5–8% of the total *Typha* biomass added was leached as DOC, 45–60% remained in the reactor as accumulated biomass, the remainder of the carbon (30–50%) exited as particulate organic carbon or was microbially respired. We hypothesized that DOC in the wastewater effluent biodegraded over the first-half of the wetland, and that DOC leaching from plant material occurred throughout the wetland. A DOC-wetland model was developed, and the results suggested that the percentage of plant-derived DOC increases with longer HRTs, and while the overall DOC concentration exiting a wetland may only be slightly lower than influent levels that a majority of the DOC, which contains a large percentage of refractory DOC, could be plant-derived. Wetlands with short HRTs would reduce the amount of DOC leached from plant material.

Key words—dissolved organic carbon (DOC), wetlands, lagoon, wastewater, modeling

INTRODUCTION

Constructed wetlands are widely used following wastewater treatment to remove nitrate, biological oxygen demand (BOD), enteric viruses, and generally improve water quality. Such low-tech treatment systems are often more economic than energy-intensive engineered treatment plants, easier to operate, and provide numerous secondary benefits (e.g. habitat enhancement). Although carbonaceous BOD reductions across wetlands have been reported, the fate of dissolved organic carbon (DOC), an unregulated parameter that has significant ecological and human health impacts, across wetlands has not been thoroughly studied.

Wastewater effluent may contain naturally occurring humic substances, biopolymers formed during wastewater treatment, and anthroprogenic compounds (e.g. pharmaceutical compounds) not removed during wastewater treatment (Rickert and Hunter, 1971; Hejzlar and Chudoba, 1986; Link *et al.*, 1989; Fujita *et al.*, 1996). DOC can provide a bacterial energy source for denitrification, complex with metals and hydrophobic organics, and reduce light penetration in water. Increasingly, especially in arid regions of the world, wastewater effluent flows can represent a large fraction or majority of the total flow in a receiving water that may serve as a downstream potable water supply or recharge groundwater aquifers used as potable water supplies. Potable water treatment generally includes chemical disinfection (e.g. chlorine), and reactions between disinfectants and DOC can form carcinogenic by-products (e.g. trihalomethanes) that regulated. Given the importance of DOC in the environment, including its significance during drinking water treatment, this paper addresses the fate and transformations in DOC through constructed wetlands receiving wastewater effluent.

Constructed wetlands for wastewater treatment are located throughout the world (Bhamidimarri *et*

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al., 1991; Reed, 1991; Haberl *et al.*, 1995; Hiley, 1995; Greenway and Simpson, 1996; Magmedov *et al.*, 1996). Wetlands have also been used to treat high strength organic loads from landfill leachate (Martin and Johnson, 1995). Free water surface and subsurface wetland systems are commonly used in the U.S., and both empirical design models and mass balance design models have been proposed (Reed, 1991; Buchberger and Shaw, 1995; Reed *et al.*, 1995; Kadlec and Knight, 1996; Knight *et al.*, 1999). Wetland systems can remove bacteria, suspended solids, BOD, nitrogen (NH_3 and NO_3^-), metals, and phosphorous. Specific water quality entering wetlands will control the design criteria. Consequently, existing wetlands are designed with a wide range of hydraulic retention times (HRTs), generally ranging from 2 to 20 days. Longer HRTs are generally employed to permit aeration via diffusion from the atmosphere for BOD removal and nitrification. Shorter HRTs are often employed when the wetlands receive higher quality treated wastewater (e.g. denitrified), and the wetlands are used for other design objectives (e.g. contaminant "polishing", habitat enhancement). Only a few studies have considered the fate of organic carbon directly, but many studies have measured changes in BOD and/or COD. Anaerobic and aerobic microbial respiration of DOC in wetlands can reduce oxygen demands by 50 to >95% across constructed wetlands (Greenway and Simpson, 1996; Kadlec and Knight, 1996). Breen (1990) presented a simple two compartment mass balance approach for modeling oxygen demand.

DOC can be leached into water flowing through wetlands as plants, algae, and bacteria grow, die and decay. During growth phases, the above-ground to below-ground ratio for plant biomass increases for *Typha*, a common wetland plant (Breen, 1990). Not all the above-ground biomass directly contacts the water; however, dying plants and plants cut by animals do contact the water and can leach DOC. Bacterial decomposition of plant detritus has been shown to convert particulate organic carbon (POC) into dissolved form and cause the release of humic substances into the bulk dissolved organic carbon (DOC) pool (Moran and Hodson, 1994). Rhizome and roots of plants can release soluble organic carbon (Schnitzer and Khan, 1972; Thurman, 1985). Thus a knowledge of the phase and rate of plant growth, amount of standing biomass, and amount of rhizome and root in the wetland may be needed to understand the cumulative effect of wetland plants on DOC production within wetlands. A conceptual view of DOC related wetland processes is schematically illustrated in Fig. 1. Wastewater effluent DOC (C_L) entering a constructed wetland undergoes biological degradation, resulting in particulate biomass growth and cellular respiration to carbon dioxide. DOC leaching (C_P) from growing and dead plants can increase DOC levels through wetlands. As a result of microbial degradation and plant leaching, the amount and composition of influent DOC can be transformed across a constructed wetland. In this paper we document the overall changes, resulting from the cumulative processes illustrated in Fig. 1, in wastewater effluent as it passes through a constructed wetland, and separately characterize DOC leached from a major pool of OC, specifically wetland plants.

The Prado Wetlands, located along the Santa Ana River in southern California, receive a mix of water supplies including secondary-treated wastewater and are used for flood control, water storage, wildlife enhancement, and nitrate treatment. Using pyrolysis GC-MS, Gray (1997) demonstrated that both the quantity and quality of the organic carbon changes across the wetland. Specific carbon "fragments" with apparent anthroprogenic origins (e.g. xylenes and chlorinated compounds) were removed while compounds associated with plant, algae, or bacteria by-products (e.g. cresols, phenols, acetmides) were

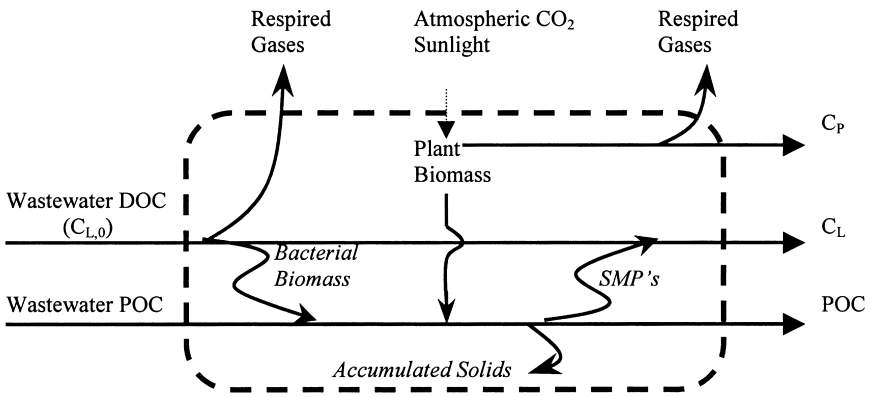


Fig. 1. Conceptual model for the transformation of the total DOC exiting a wetland, comprising both lagoon-origin DOC (C_L) and plant-derived DOC (C_P) (SMP = Soluble microbial products).

formed. This work represents the potential for DOC transformations to occur in wetlands.

Reuse of wastewater as direct or indirect sources of drinking water has been increasing worldwide, especially in drier climates like the southwestern U.S.. Both high-tech (e.g. reverse osmosis) and low-tech (e.g. wetland treatment followed by groundwater recharge) treatment options have been employed. The fate, characteristics, and reactivity of DOC toward disinfectants in both high- and low-tech wastewater reuse schemes is of critical importance (Wilson *et al.*, 1995; Quanrud *et al.*, 1996). Trace organic contaminants are one concern. The potential for DOC to react with disinfectants (e.g. chlorine) and form carcinogenic and regulated by-products (e.g. trihalomethanes) poses significant health concerns for reuse of the wastewater. There is a need to understand how constructed wetlands alter DOC characteristics, and how they affect subsequent treatment processes (e.g. biological degradation potential during groundwater recharge).

The goal of this paper is to characterize the amount, structure, and reactivity of DOC in lagoon-treated wastewater effluent as it is transformed along a longitudinal gradient through a constructed wetland. The amount of DOC leaching and characteristics of one specific source of DOC, namely DOC leaching from decaying wetland plant material (*Typha*), was investigated in laboratory continuous-flow reactors. A conceptual model was developed to represent hypothesized major sources/sinks for DOC in a constructed wetland. Sequential nitrogen removal, and its relationship with organic carbon in constructed wetlands, is discussed in a companion and related paper (Ingersoll and Baker, 1998; Gerke *et al.*, in review).

EXPERIMENTAL METHODS AND ANALYTICAL PROCEDURES

Experimental methods

Full scale constructed wetland site description (Kingman wetland). Constructed treatment wetlands in Kingman Arizona were built 1992 (Manthe and Ash, 1993). The 9-hectare wetland treatment system consists of three equal-sized cells (700 × 50 m) connected in series (Fig. 2). The shallow zones (~0.2 m deep) were planted with *Scirpus* in 1994. Each cell is transected by two internal deep zones (1 m in depth) and includes an open pool near each outlet. These features reduce hydraulic short circuiting through the wetland. At the time of the study (1996–1997), wetland vegetation was a well-established mixture of bulrushes (*Scirpus*) and cattails (*Typha*). The deep zones remained free of emergent vegetation. Wetland vegetation was deliberately burned in January 1997, to remove accumulated plant material. Measured dried weight of standing crop biomass in 0.1 m squares averaged 3.0 kg DW/m^2 in June, 1997, and 1.8 kg DW/m^2 in August, 1997 (Gerke and Baker, 1998). The carbon content of the dried plant material was taken as 50% of total weight as per Boyd and Hess (1970).

The wetland received nonnitrified lagoon effluent from aerated lagoons that treat municipal wastewater for the city of Kingman, AZ. Flow into the wetland averaged 3710 m^3/day and was reasonably constant throughout the year, varying from 3190 to 4415 m^3/day. During our study, the average hydraulic retention time was approximately 10 days and the wetlands had an average hydraulic loading rate of 4.1 cm/day.

The primary purpose of the wetlands is for the removal of nitrogen to levels below EPA regulations for recharge to groundwater (10 mg/L N–NO_3). The lagoon treatment process upstream of the wetland has a HRT of 15 days and its effluent contained roughly 60 mg/L BOD, total nitrogen of 34 and 24 mg-N/L ammonia. During the study period nitrogen removal efficiency averaged 75% across the wetland system (Gerke and Baker, 1998; Gerke *et al.*, submitted for publication), and the nitrate MCL was routinely met. Discharge from the constructed wetlands is conveyed to several infiltration basins that recharge local groundwater. Grab water samples were collected at thirteen locations along the longitudinal axis of the three wetland cells, and analyzed for the amount, structure, and reactivity of DOC.

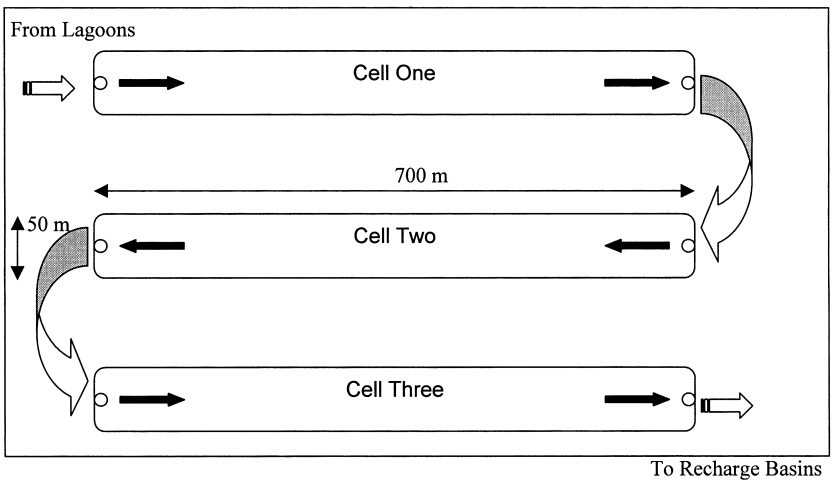


Fig. 2. Schematic of constructed wetlands in Kingman, AZ.

Wetland microcosms. A laboratory apparatus (Fig. 3) was used to simulate the leaching of organic carbon from dried cattails. Eight acrylic tanks (20 × 25 × 13 cm), each with a 6.4 L volume, from a previous wetland microcosm study focusing on nitrate removal were used (Ingersoll and Baker, 1998). A baffle within each tank limited short-circuiting. A model feed water was pumped (Monistat cassette peristaltic pump) through several microcosms at three different flowrates to achieve HRTs of 1.6 (m = 4), 2.7 (m = 2) and 7.4 (m = 2) days. Flowrates were measured weekly. The feed water comprised distilled water plus salts and nutrient constituents (0.16 mM K_2HPO4, 1 mM NH_4Cl and 0.6 mM $CaCO_3$). The final DOC of the feed water was 0.98 mg/L. Dried, chopped cattails collected from the Kingman wetlands was added weekly at a rate of 2.24 g per tank, corresponding to a loading rate of 4500 g/m^2/year (Ingersoll and Baker, 1998).

All eight microcosms were operated for a period of 14 weeks until a steady-state condition, defined as constant DOC and UVA for 3 consecutive weeks, was achieved. Half of the microcosms were removed; DOC concentrations and the volume of water in each reactor was measured. The four remaining microcosms were operated at steady-state conditions, adding 2.24 g/week dried cattails, for an additional 2 months. Samples of influent and effluent water from the microcosms were sampled twice per week and analyzed for the amount, structure, and reactivity of DOC.

Analytical procedures

Dissolved organic carbon (DOC) concentration. All DOC measurements were conducted on samples that were filtered with preashed Whatman GF/F filters and stored at 4°C in acid-washed and ashed (550°C) amber glass bottles. Samples were acidified to pH 2 with hydrochloric acid (HCl). Nonpurgeable DOC was measured by combustion (680°C) on a platinum catalyst with CO_2 detection using a Shimadzu TOC 5050A analyzer (Sugimura and Suzuki, 1988). Potassium hydrogen phthalate (Shimadzu Inc. reagent stored in desiccator) standards of 1, 3, 5 and 15 mg/L were prepared daily. Samples were run in triplicate, or until the coefficient of variation was less than 3%.

DOC structure. Ultraviolet adsorption at 254 nm (UVA_{254}) measurements were performed with a Shimadzu 1601 UV-Vis spectrophotometer using a 1 cm quartz cell, and Super-Q (Millipore Inc.) water as a blank. All samples were acidified to pH 2 with HCl prior to analysis. Specific UVA (SUVA, m^{-1} $(mg/L)^{-1}$) value was calculated by dividing the UVA_{254} measurement by the DOC concentration. Since UVA measurements near 254 nm measure sp^2-hydrbidized carbon–carbon double bonds, increasing SUVA correlates with increasing aromatic carbon content and molecular weight for DOC (Chin *et al*., 1994).

Selective samples were also analyzed by fluorescence spectroscopy, XAD8 chromatography into hydrophobic acid (fulvic substances) content, and ^{13}C-NMR on desalted and lyophilized XAD8 isolates. Fluorescence spectra were obtained using a Shimadzu 551 with PC control at an excitation wavelength of 360 nm and an emission spectrum of 400–600 nm. XAD8 chromatography was used to fractionate and concentrate fulvic acids from DOC according to established methodologies (Aiken *et al*., 1992). In brief, samples were adjusted to pH 2.0 and passed through a glass column containing XAD8 resin, and then eluted with 0.1 N NaOH, desalted (MSC-1-H resin), and lyophilized. A mass balance on carbon was performed and the percentage of carbon eluted was used to calculate the percentage of fulvic acid content.

DOC reactivity. The chemical and biological reactivity of DOC was assessed. The trihalomethane formation potential (THMFP) was used to assess the chemical reactivity of DOC towards disinfectants. A free-chlorine dose of 5 mg Cl_2/mg DOC was added, above a 7 mg Cl_2/mg NH_4, and allowed to react (40 ml amber glass bottle with Teflon septa) for seven days in the dark at 25°C. All chlorination was performed in duplicate and the average THMFP value reported. After seven days the chlorine was measured (DPD colorimetric method) and quenched to a final Na_2SO_3 concentration of 3.8 mM. THMs were extracted (8 g NaCl plus 3 mL MTBE) from 30 mL of chlorinated water. THMs in the MTBE phase were measured with a Hewlett Packard 5890 GC. Standards (Supelco) were made over a wide range (0, 25, 50, 100, 250, 500 and 750 μg/L) for each THM specie. THMFP represents the additive concentration of $CHCl_3$, $CHCl_2Br$, $CHClBr_2$ and $CHBr_3$.

The lability, or biological reactivity, of the DOC was measured using biologically active sand in a 1 L glass batch reactor based upon established methodologies (Allegeier et al., 1996). The rate of DOC disappearance in the bioreactor was measured over a seven day period. The amount of biologically degradable organic carbon ($BDOC_7$) was taken as the difference between initial and final DOC values. Kinetic DOC disappearance was fit with a first-order decay equation ($DOC = DOC_0^* EXP(-k_{bio}t)$), where k_{bio} is a first-order rate constant (day^{-1}). BDOC tests were conducted in duplicate, at a minimum.

RESULTS AND DISCUSSION

DOC transformations through Kingman wetlands

Amount of DOC. Lagoon-treated wastewater DOC was transformed across the constructed wetlands. DOC levels were monitored at several locations in each of three, equal-sized wetland cells.

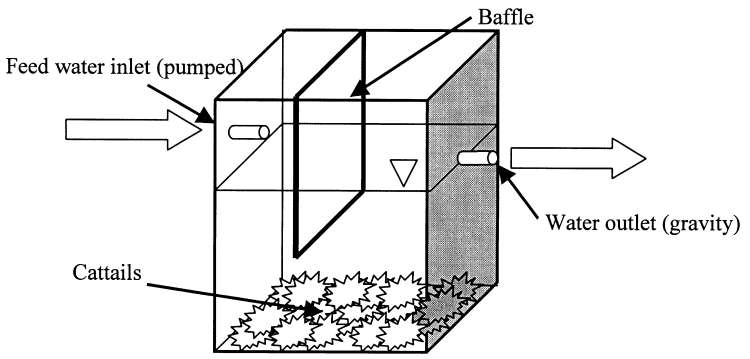


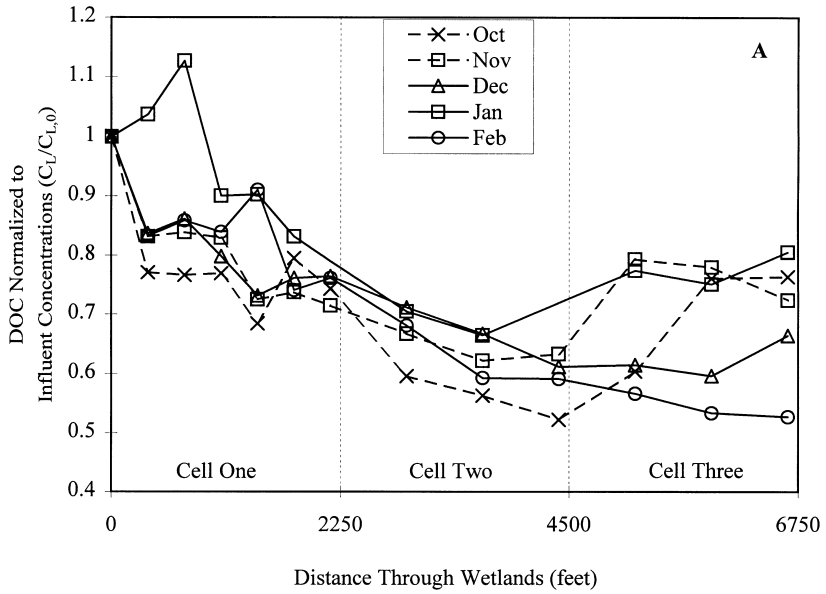
Fig. 3. Schematic of wetland microcosm reactors.

Table 1. transformations in DOC concentrations across each wetland cell (Kingman, AZ) and proposed DOC mechanisms

	DOC_{in}[a] (range) (mg/L)	DOC_{out}[a] (range) (mg/L)	Percent change[b] (range) (%)	Dominant mechanism
Cell one	20.4 (16.9 to 25.3)	15.0 (12.2 to 19.7)	−26 (−17 to −40)	biodegradation
Cell Two	15.0 (12.2 to 19.7)	13.3 (8.81 to 17.1)	−12 (−30 to +9)	biodegradation and leaching
Cell Three	13.3 (8.81 to 17.1)	14.7 (11.3 to 19.1)	+13 (−11 to +46)	leaching

[a]Average values (n = 10); the value of one standard deviation (n = 10) was 2.95, 2.37, 2.64 and 2.54 mg/L for DOC_{in} to each of the three cells and DOC_{out} from cell three, respectively.
[b]Percent change calculated as $(DOC_{in}-DOC_{out})/DOC_{in} \times 100$.

In all cases, DOC levels exiting the wetland were less than the DOC levels entering the wetland. The average (n = 10) DOC level entering ($C_{L,0}$) the wetland from the lagoon-treatment process, was 20.4 mg/L (Table 1). DOC_{in} and DOC_{out} in Table 1 represent DOC levels at the entrance and exit of each wetland cell, respectively; $C_{L,0}$ is equivalent to DOC_{in} for Cell One. The average (n = 10) effluent



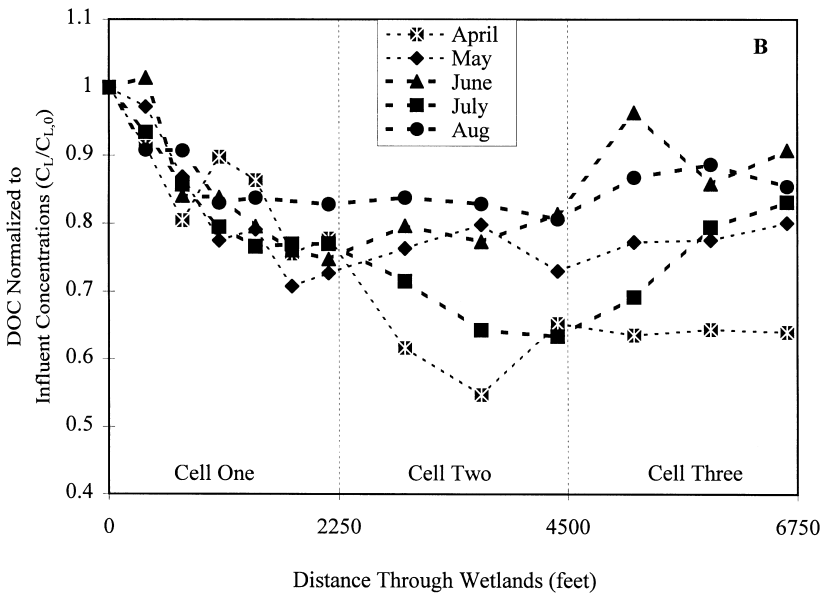


Fig. 4. Spatial and temporal normalized DOC levels (normalized to DOC_{INLET}) across the Kingman, AZ, wetlands (HRT ~12 days) during the months of (A) October through February and (B) April through August.

DOC level from the wetlands was 14.7 mg/L (range: 11.3–19.1 mg/L). Since $C_{L,0}$ changed during the year, DOC values along a longitudinal gradient through the wetlands were normalized to $C_{L,0}$ for each month (Fig. 4). Changes in DOC through each cell are discussed below. Notable seasonal patterns were observed. Overall through the wetland, DOC levels decreased the most during the winter (November through April) and decreased to a lesser extent during the summer when little wetland plant growth occurred. DOC removal probably occurred due to slow biological processes, similar to those that may occur in an extended lagoon wastewater treatment system with a very long HRT. During summer months with active plant growth, DOC values decreased across cell one and increased through the remaining cells.

The majority of the DOC removal occurred in cell one of the wetlands (Table 1). On average, DOC concentration decreased 26% across cell one. All months had similar removal levels. We hypothesize that biodegradation is the dominant DOC mechanism in Cell One.

DOC levels generally decreased by across cell two, except during May and June. During the months of April through July a notable qualitative

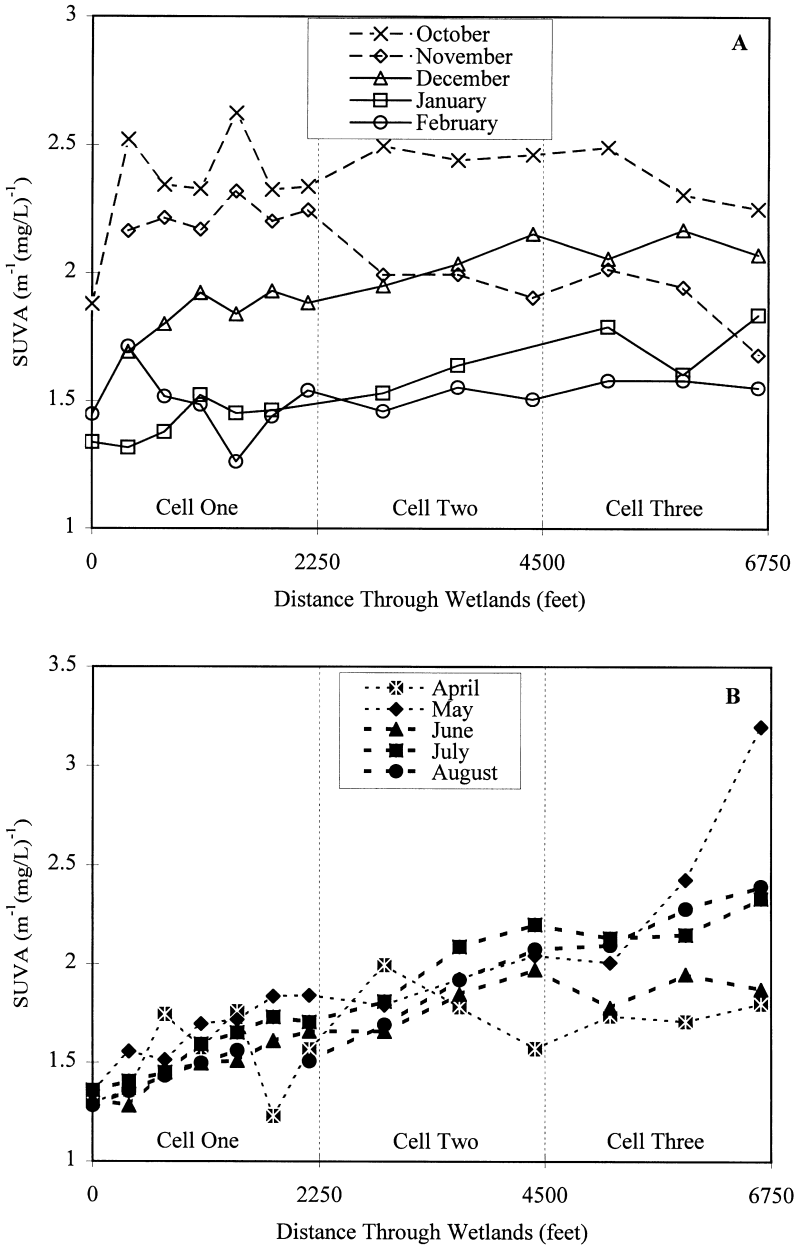


Fig. 5. Spatial and temporal SUVA values across the Kingman, AZ, wetlands (HRT ~12 days) during the months of (A) October through February and (B) April through August.

increase in the height and "greenness" of plants in the wetland was noticed. Lower removal rates were observed during these periods. We hypothesize that DOC continued to degrade across cell two, more slowly than in cell one. Furthermore, DOC leaching from actively growing plants may be occurring during the summer.

DOC levels generally increased across the final wetland section (cell three). The only exception was February and April, months immediately after the standing crop was burned as part of the wetland management program (January, 1997). Consequently, the wetland contained a small amount of biomass during these months. DOC decreased by 11 and 2% across Cell three in February and April, respectively. On average, the DOC increased 18% across cell three, excluding February and April. The largest increases in DOC ($>30\%$) occurred in July and October. We hypothesize that the increase in DOC levels across cell three resulted as a consequence of DOC leaching from wetland plant materials.

DOC release (i.e. leaching) from plants and detritus probably occurs in all the wetland cells, therefore the rate of removal of the overall DOC decrease is a relative rate. DOC leached from decaying plants may itself degrade biologically. Given the large changes in DOC across cell one, presumably due to biodegradation of DOC in the lagoon-treated wastewater effluent (discussed later), the effects of plant leaching is masked and not as important in transforming DOC, relatively, as the plant leaching process is in Cell Two and Three.

Change in structural characteristics of DOC. Overall, UVA_{254} decreased through the wetlands. However, DOC values decreased to a greater extent than UVA_{254}. Therefore, SUVA values increased across the wetland, except during November (Fig. 5). SUVA entering the wetlands ranged between 1.3 and 1.9 m^{-1} $(mg/L)^{-1}$. After wetland treatment, SUVA increased to an average value 2.1 m^{-1} $(mg/L)^{-1}$ with a wide range of monthly SUVA values from 1.5 and 3.3 m^{-1} $(mg/L)^{-1}$. On average, SUVA increased by 50% ($n = 10$) across the wetland. The largest increase in SUVA occurred within the first cell (Table 2), where SUVA increased by an average of 26%. We hypothesized that labile carbon was biodegraded in Cell One. The biodegraded carbon presumably comprised lower in molecular weight and less aromatic DOC. Therefore, preferential removal of labile DOC resulted in an increased SUVA.

SUVA continued to increase across cells two and three. During the months of May through August SUVA values exhibited the largest increases (42–135% increases SUVA entering the wetland). We hypothesized that in addition to preferential biodegradation of labile DOC contained in the wastewater effluent, leached plant material entered the wetland water. The SUVA of leached cattail material (2.3 m^{-1} $(mg/L)^{-1}$ for 7.4 day HRT leaching, discussed later) is higher than the SUVA of the wastewater entering the wetland (1.4 ± 0.2 m^{-1} $(mg/L)^{-1}$).

Although a significant amount of fluorescence data was collected, the most useful data was obtained by contrasting spectra properties for DOC at the inlet against the outlet for the wetlands. Table 3 summarizes the findings. In order to account for variable DOC levels, a fluorescence index (FI) was calculated to present the general shape of a fluorescence emission spectra. Previous work has suggested that a FI > 2.0 is indicative of microbially derived fulvic acids and a value less than 1.5 represents more lignin- or terrestrially-derived fulvic acids (McKnight *et al*., in press). During each month of wetland sampling, FI values decreased slightly across the wetland. Although the percentage change is small, this could suggest preferential removal of DOC. However, we hypothesize that DOC is leaching from plants, resulting in a reduction of FI that is indicative of greater fraction of lignin-derived organic material.

During a period when plant leaching was predicted to be important (June 1998) samples from the inlet ($C_{L,0} = 24$ mg/L) and outlet ($C_L = 14$ mg/L) of the Kingman wetland were collected for fulvic acid analysis. The percentage of DOC retained by XAD8 resin increased from 37 to 44% across the wetland. We have found similar results in other wetlands that receive denitrified effluent, and the results suggest that the DOC is more hydrophobic in nature leaving the wetland compared against the material entering the wetland.

Wetland microcosms

Wetland microcosms were operated at three hydraulic retention times (HRTs), with weekly additions of chopped, dried cattails, in order to quantify the amount of DOC leached in wetlands

Table 2. Transformations in SUVA (m^{-1} $(mg/L)^{-1}$) across each wetland cell (Kingman, AZ)

	$SUVA_{IN}$[a] (range)	$SUVA_{OUT}$[a] (range)	Percent change average[b] (%)
Cell 1	1.41 ± 0.20 (1.28 to 1.88)	1.78 ± 0.30 (1.51 to 2.34)	+26
Cell 2	1.78 ± 0.30 (1.51 to 2.34)	1.96 ± 0.30 (1.51 to 2.46)	+11
Cell 3	1.96 ± 0.30 (1.51 to 2.46)	2.10 ± 0.48 (1.55 to 3.20)	+7

[a]Average value plus/minus value of one standard deviation ($n = 10$).
[b]Percent change calculated as $(DOC_{in} - DOC_{out})/DOC_{in} \times 100$.

Table 3. Fluorescence index values for wetland inflow and outflow[a]

Sampling Date	Wetland inlet FI value	Wetland outlet FI value	Percentage change in FI value (%)
October 1996	1.91	1.78	−7
November 1996	1.87	1.80	−4
December 1996	1.93	1.77	−8
January 1997	1.99	1.79	−10
February 1997	1.89	1.87	−1
April 1997	1.82	1.71	−6
June 1997	1.76	1.60	−9
July 1997	1.77	1.59	−10

[a]FI is computed by dividing the fluorescence emission intensity at 450 nm by that at 500 nm using an excitation wavelength of 370 nm.

and to characterize leached wetland DOC structure and reactivity. The mechanisms responsible for DOC leaching were likely a combination of both microbial degradation of plant material plus abiotic solubility of plant organic carbon compounds. DOC and SUVA values *after* reaching steady-state conditions are presented in Fig. 6, and summarized in Table 4. Duplicate experimental data from microcosms with 1.6 day HRTs were not statistically different ($p < 0.05$). Longer HRTs resulted in statistically higher values of leached DOC, and higher SUVA values ($p < 0.005$ based on ANOVA analysis). Based upon this data, the observed increase in SUVA across the full-scale wetland (Fig. 5) may have been in part due to the longer retention times with distance in the wetland.

The yield of DOC leached from cattails was also calculated. A mass leaching graph from the microcosms, after reaching steady-state conditions, is shown in Fig. 7. Mass leaching is a function of DOC concentration and flowrate. The flowrate varied for each HRT, since equal volume reactors were used to simulate each HRT. A linear regression through the data in Fig. 7 yielded mass leaching constants (k_{PL}, mg DOC leached per g dried cattails added) from 58 to 84 mg/g (i.e. 5.8–8.4% of carbon added). The regressions fit the data well, except for the initial part of one duplicate microcosms with a 1.6 day HRT. Values for the leaching constants decreased slightly with increasing HRT, with the 7.4 day HRT having a 30% lower k_{PL} value compared against the 1.6 day HRT microcosm. Although the microcosms had different DOC concentrations, all the microcosms leached comparable levels of organic carbon on a mass basis.

The accumulated biomass in the microcosms were measured at the beginning of steady-state conditions, by sacrificing four microcosms with varying HRTs, and fifty six days later at the end of the steady-state experiments. During the fifty-six day steady-state operation a total dry *Typha* biomass of 8.96 gC was added to each reactor. Roughly 5–8% (0.50–0.70 gC) was leached and measured as DOC (Fig. 7). The amount of biomass that accumulated in the microcosms during the fifty-six day steady-state experiment ranged between 45 and 60% ($n = 4$) of the *Typha* biomass added. The unaccounted for organic carbon (35–60%) exited the microcosms either as particulate organic carbon or through metabolism to carbon dioxide and possibly methane; neither POC nor respiration gases were directly measured. However, the importance of these results were that relative to other carbon pools, the amount of plant organic carbon leached as residual DOC is small, but as a percentage of DOC present in waters the incremental DOC increase due to plant leaching may be relevant.

DOC BIOLOGICAL AND CHEMICAL REACTIVITY

Lability of organic carbon in wetlands

The relative ability for DOC to be biologically assimilated (sorption and/or degradation) was assessed using batch biologically degradable organic carbon (BDOC) reactors. The results of $BDOC_7$ tests for five different wetland-related waters are shown in Table 5. The DOC levels decreased from an initial value, DOC_I, to a final value, DOC_F, after seven days. $BDOC_7$ was computed as the difference between DOC_I and DOC_F. The lagoon-treated water (wetland influent) contained 21.8 mg/L DOC, of which 66% was labile

Table 4. DOC concentrations and SUVA for wetland microcosms effluents under steady-state conditions

	Reactor HRT (days)			
	1.6 days	1.6 days (duplicate)	2.7 days	7.4 days
DOC (mg/L)				
Average	2.90	2.79	4.75	10.5
Standard Deviation	1.23	0.71	1.06	1.35
SUVA $(m^{-1}\ (mg/L)^{-1})$				
Average	1.55	1.69	1.80	2.31
Standard Deviation	0.32	0.27	0.24	0.31

($BDOC_7 = 14.4$ mg/L). The effluent from the wetland, which we hypothesized would contain nondegraded wastewater DOC plus leached wetland plant DOC, had a DOC of 13.3 mg/L, of which 37% was labile ($BDOC_7 = 4.94$ mg/L). Net DOC removal across the wetland was 40%, whereas net removal of labile DOC was 65%. Therefore, wetlands appear to preferentially remove labile DOC.

Increasing HRTs for the microcosms resulted in higher $BDOC_7$ values. However, the percentage of $BDOC_7$ was similar for each retention time ($33 \pm 4\%$). It was interesting to note that the microcosm

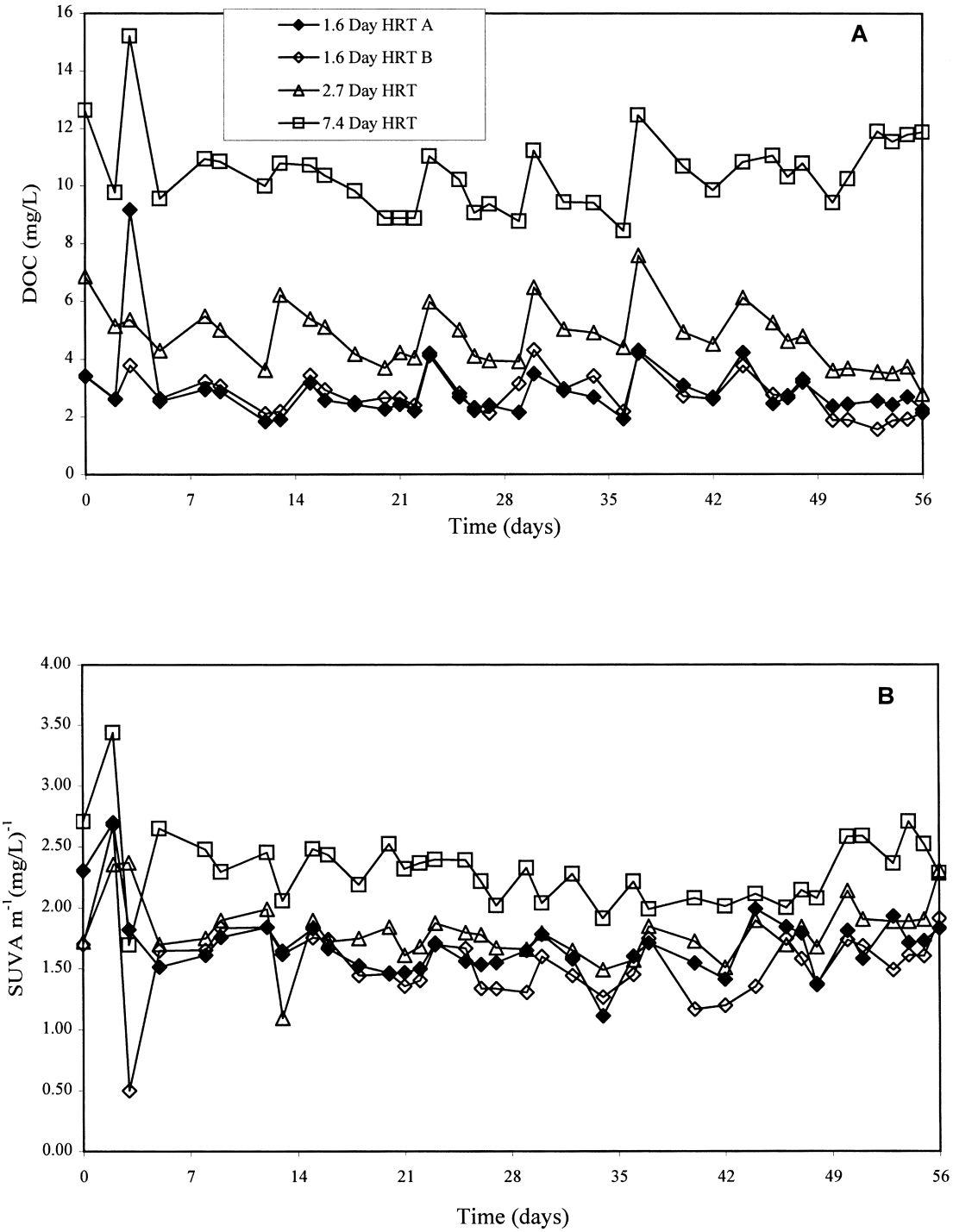


Fig. 6. Steady-state levels exiting wetland microcosms at three different HRT's for (A) DOC concentrations and (B) SUVA values (duplicate microcosms for 1.6 day HRT).

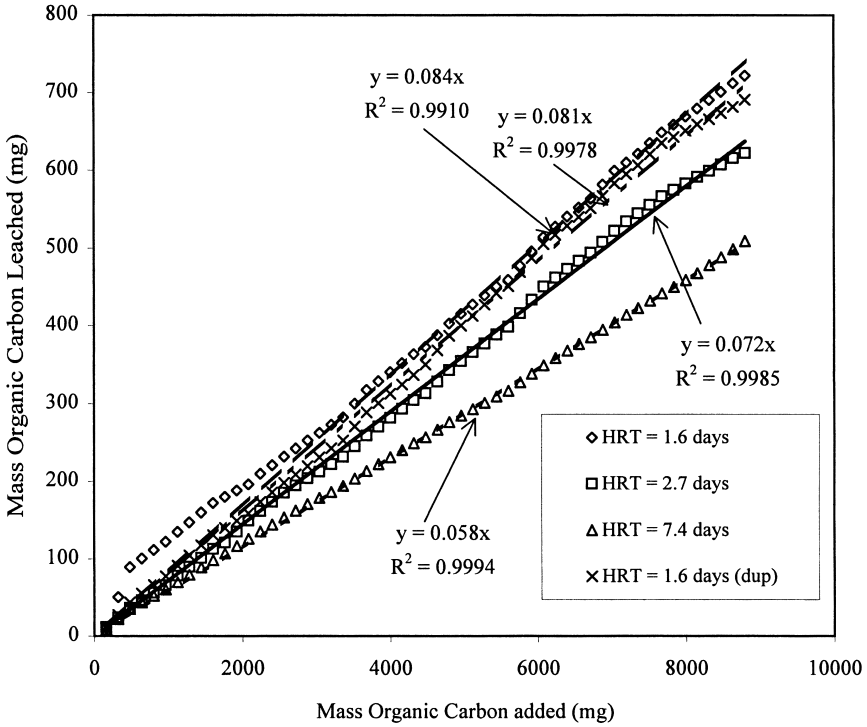


Fig. 7. Cumulative mass of dissolved organic carbon leached from dried *Typha* plant material and linear regressions for the leaching constants.

effluent and wetland effluent contained roughly the same percentage of $BDOC_7$ and similar DOC_F (i.e. nonlabile, refractory) levels (Table 4). This could suggest that the majority of nonlabile DOC in the wetland outlet water is comprised of leached plant material.

SUVA values changed during the BDOC tests (Table 5). For the Kingman, AZ, samples, a larger decrease in SUVA was observed after biodegradation (seven-day BDOC reactors) of the wetland influent sample compared against the change for the wetland effluent sample. This could suggest that organic material with a lower SUVA value was preferentially removed. Since SUVA increased, larger molecular weight and more aromatic compounds tended not to be preferentially removed via biodegradation. Overall, the changes in SUVA values for the microcosms were small and no apparent trends existed.

First-order rate constants (k_{Bio}) were calculated from kinetic data for DOC biodegradation (BDOC reactors). DOC was measured in triplicate reactors over the course of a seven-day BDOC experiments and rate data was fitted to the observed data (Figs. 8 and 9). The calculated k_{Bio} values for the microcosm effluent increased slightly with longer HRTs from $1.9 \times 10^{-3}\,day^{-1}$ (HRT = 1.6 days) to $2.6 \times 10^{-3}\,day^{-1}$ (HRT = 2.7 days) and $2.8 \times 10^{-3}\,day^{-1}$ (HRT = 7.4 days). These k_{Bio} values were lower than those obtained from the wetland inlet and outlet water (March 1998). The value of k_{Bio} decreased from $6.2 \times 10^{-3}\,day^{-1}$ in the wetland inlet to $3.1 \times 10^{-3}\,day^{-1}$ in the wetland outlet, representing a decrease in the biodegradable nature of DOC exiting the constructed wetland. Overall, the value of

Table 5. Assessment of lability of organic carbon in wetlands

System	Variable parameters	DOC_I (mg/L)	DOC_F (mg/L)	$BDOC_7$ (mg/L)[a]	Percent BDOC[b] (%)	% Change SUVA[c] (%)
Kingman Wetlands (March 1998)	inlet	21.8	7.40	14.4	66	+86
	outlet	13.3	8.33	4.94	37	+16
Microcosms (after steady-state)	HRT = 1.6 days	2.84	2.01	0.83	29	−6.0
	HRT = 2.7 days	3.55	2.41	1.2	32	+12
	HRT = 7.4 days	11.8	7.57	4.3	37	−0.81

[a] $BDOC_7 = DOC_I - DOC_F$.
[b] Calculated as $(DOC_I - DOC_F)/DOC_I \times 100$.
[c] Calculated as $(SUVA_I - SUVA_F)/SUVA_I \times 100$.

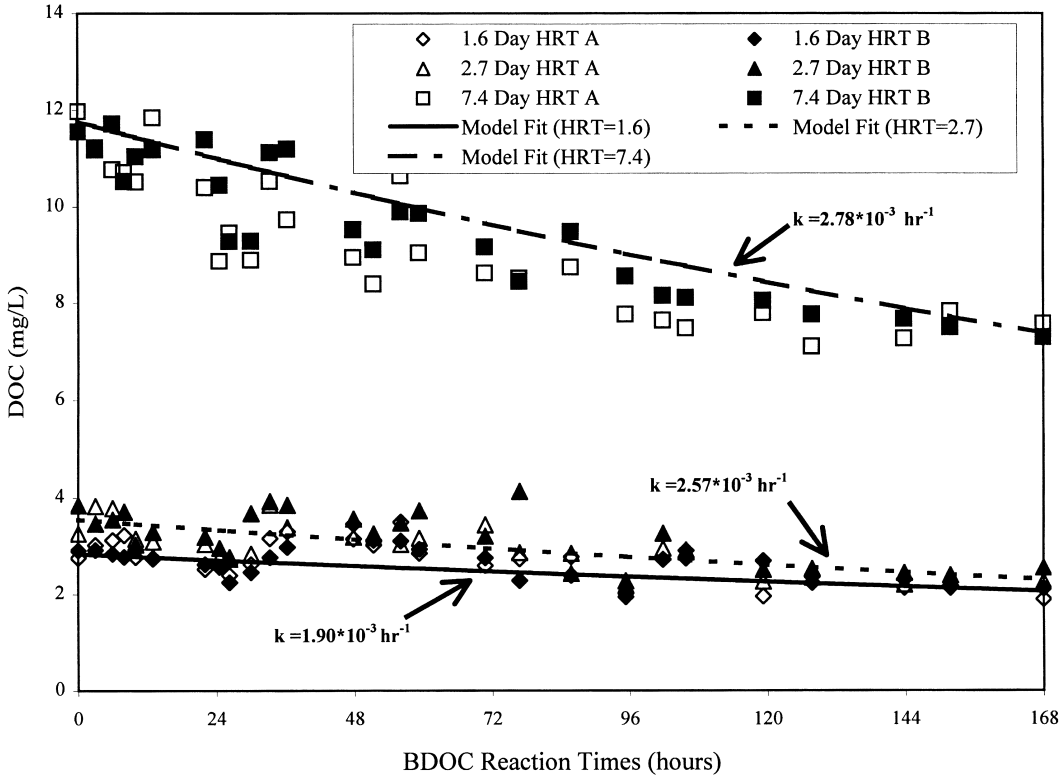


Fig. 8. Biological degradation data and fitted curves for DOC material leached from *Typha* in microcosms with three different HRTs (duplicate BDOC experiments shown in open and closed symbols).

k_{Bio} for the lagoon treated wastewater DOC was roughly twice that of plant-leached DOC, and the k_{Bio} of the wetland effluent was similar to that of plant-leached DOC.

Chemical reactivity of DOC

Trihalomethane formation potential (THMFP) tests were performed on the wetlands and microcosms waters to assess the changes in chemical reactivity (Table 6). The averages of duplicate chlorination and duplicate analysis are presented. THMFP increased with longer retention time of the microcosm water due to increase DOC levels. The specific reactivity (THMFP/DOC) of DOC for forming THMs were higher for the plant-leached DOC from the microcosms in comparison to the water samples from the wetlands. Although the specific reactivity values for the samples tested are similar to those for drinking waters (30–60 μg TTHM/mg DOC), the DOC (mg DOC/L) values in the wetland systems are considerably higher than drinking waters. Consequently, direct use of wetland effluent as a drinking water supply would require significant pretreatment prior to potable use in order to avoid exceeding MCL limits on THMs. This is one reason why Kingman practices surface infiltration, since natural soil aquifer treatment (SAT) processes are reported to significantly lower DOC values (Amy *et al.*, 1993; Pinney, 1998).

Table 6. THMFP of constructed wetland and microcosm waters

System	DOC (mg/L)	TTHMFP (μg/L)	TTHM/DOC (μg TTHMs/mg DOC)
Wetlands			
Entering	21.5	857	40.0
Exiting	12.5	447	35.9
Microcosms			
1.6 day HRT	2.19	104	47.7
2.7 day HRT	2.78	174	62.7
7.4 day HRT	11.9	698	58.9

MODELING DOC IN WETLANDS

A mass balance model was developed to illustrate the potential sources and fate of DOC in wetlands receiving wastewater effluent. The mass balance model is only for DOC and represents a portion of the overall carbon mass balance as illustrated in Fig. 1. First, DOC leaching from plants and subsequent DOC biodegradation was modeled. Predicted DOC levels were compared against observed microcosm DOC data as a function of residence time. Then additional terms were added to simulate lagoon effluent entering a wetland.

The mass balance on the concentration (C_P) of DOC originating from plant leached organic carbon can be expressed as follows:

$$V\frac{dC_P}{dt} = QC_{P,0} - QC_P + YA - k_P C_P V, \quad (1)$$

where V is the volume of water in reactor/wetland (m^3), Q is the flowrate (m^3/day), $C_{P,0}$ is the initial concentration of plant-derived DOC entering the reactor/wetland ($C_{P,0}$ was set to zero), Y is the DOC loading rate (g soluble C/day m^2), A is the reactor/wetland surface area (m^2) and k_P is the first-order rate constant for plant-derived DOC biodegradation (day^{-1}) based upon kinetic BDOC tests. The DOC loading rate (Y) was estimated using the observed *Typha* mass leaching constant ($k_{PL} = 0.08$ g DOC per g C *Typha* added), the rate of biomass (B) expressed as carbon mass added (C_{added}), and the following relationship:

$$Y = \left(\frac{k_{PL}(\text{g DOC})}{\text{g } C_{added}}\right)\left(\frac{B \text{ g } C_{added}}{d}\right)\left(\frac{1}{A(m^2)}\right). \quad (2)$$

At steady-state, the concentration of plant-derived DOC (C_P) can be calculated by the following expression:

$$C_P = \frac{Y}{(D/\tau) + k_P D}, \quad (3)$$

where D is the depth of the wetland (m) calculated as V divided by A and τ is the hydraulic residence time (d) calculated as V divided by Q.

Values for C_P based on the conditions applied to the wetland microcosms were predicted as a function of HRTs. Predicted C_P values compared well against the average observed DOC levels for the microcosm effluent (Fig. 10). The predicted C_P levels were only 1% higher than the observed average DOC value for the 1.6 day HRT. C_P was 29% higher than the 2.7 day HRT average DOC value, 14% lower than the 7.4 day HRT average DOC value. The combination of k_{PL} and k_P values lead to a reasonable agreement between predicted and observed data for the microcosms.

The next modeling step involved simulating a wetland receiving lagoon-treated wastewater. The mass balance on the concentration of lagoon-derived DOC (C_L) and subsequent degradation can be represented by the following relationship:

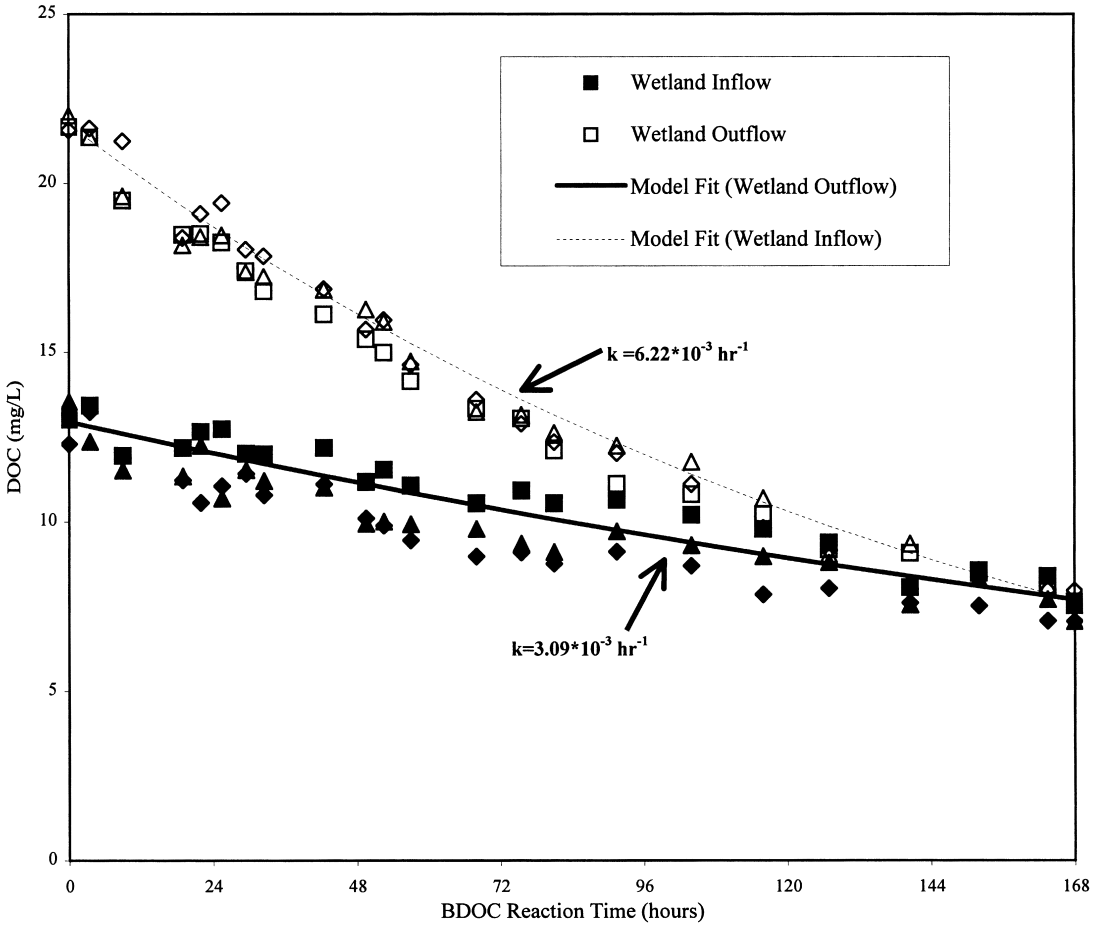


Fig. 9. Biological degradation data and fitted curves for DOC material collected at the inlet (open symbols) and outlet (closed symbols) from the Kingman, AZ, wetlands in March 1998 (triplicate BDOC experimental data shown with different symbols).

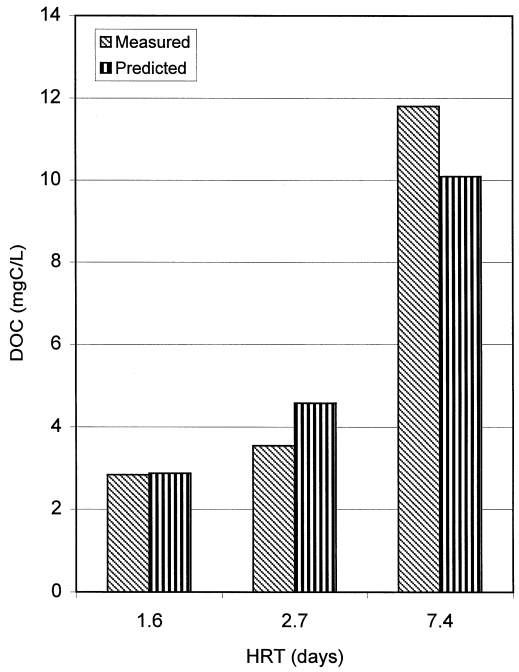


Fig. 10. Comparison of observed average DOC from wetland microcosms and predicted (Eq. (3)) DOC concentrations (Y = 0.49 g/dm^2, k_P = 0.060 d^{-1}, k_{PL} = 0.08 g/g, D = 0.25 m).

$$V\frac{dC_L}{dt} = QC_{L,0} - QC_L - k_L C_L V \quad (4)$$

Assuming steady-state conditions, C_L can be estimated as a function of residence time:

$$C_L = \frac{C_{L,0}}{1 + k_L \tau}, \quad (5)$$

where $C_{L,0}$ is the initial concentration of lagoon treated DOC entering the wetland, and k_L is the first-order rate constant for degradation of lagoon DOC. Overall, in a wetland the total concentration of DOC (C_T) would be represented as the sum of C_P and C_L.

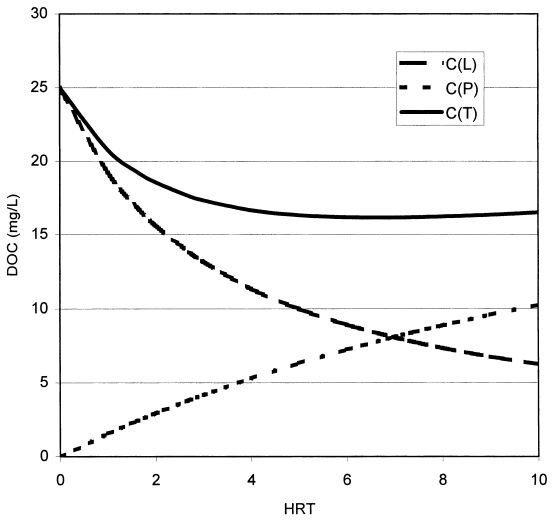


Fig. 11. Predicted lagoon-derived, plant-derived, and total DOC levels across a representative wetland (Y = 0.5 g/day m^2, k_P = 0.060 d^{-1}, k_{PL} = 0.08 g/g, k_L = 0.3 day^{-1}, $C_{L,0}$ = 25 mg/L, A = 90,000 m^2, D = 0.3 m)

Due to the lack of measured field data (e.g. monthly rates of submerged biomass additions, temperature dependent degradation rate constants, etc.), the model was not intended to simulate the Kingman, AZ, wetland. Rather the model was developed as a tool to assess the potential transformations of DOC through a constructed wetland. Predictions of C_L, C_P and C_T across a constructed wetland are illustrated in Fig. 11. Although lagoon-derived DOC decreased by 75% removal over 10 days, the overall DOC only decreased by 33%. Plant-derived DOC accounted for 10.4 mg/L after 10 days, or 62% of C_T. The predicted C_L and C_P concentrations were equal for a retention time near seven days. Increasing residence times in wetlands will lead to more plant-derived DOC. Thus although DOC concentrations only decrease slightly across the wetland, the composition of the DOC can undergo a considerable shift in composition due to DOC leaching from plant material.

SUMMARY AND IMPLICATIONS

Transformations in the amount, structure, and reactivity of DOC through a constructed wetland system were observed and simulated. Separate work with lab-scale microcosms provided insight into the rate, amount, structure, and reactivity of DOC leached from wetland plants in the absence of wastewater. The following results were observed and insights gained:

- Lagoon-treated wastewater contained a significant portion of labile DOC that was probably easily removed through a constructed wetland.
- Increasing HRTs for wetland microcosms resulted in higher DOC levels, but similar overall yields of carbon leached as DOC from *Typha* wetland plant material. In the full-scale wetland, DOC leaching from plant materials appeared more dominant during warm months with active plant growth.
- SUVA values increased slightly through the wetland and could reflect the removal of more labile, lower molecular weight DOC plus the addition of lignin-rich plant derived DOC.
- DOC reactivity (THM/DOC) toward chlorine did not change significantly across the constructed wetland, and the THM/DOC values (40–60 μg/mg) were similar to those reported for potable waters.
- The modeling suggested that wetlands with longer HRTs will result in a larger percentage of the DOC comprised of plant-derived material, rather than DOC of wastewater origin. These

results were encouraging when considering the potential for wetland effluent to be discharged to a raw drinking water supplies (surface or ground waters).

The results from this work will be important for the design constructed wetlands. Wetlands with shorter HRTs will experience less DOC leaching from plant material, compared to longer HRT designs. Many wetlands are currently designed for nitrogen removal. Short HRTs can be employed for nitrate removal, while longer HRTs are required for removing ammonia, since the later requires oxidation of ammonia to nitrate prior to removal as nitrogen gas. Therefore, the greatest impact of DOC leaching will likely be experienced in constructed wetland systems with longer HRTs, such as those used when ammonia removal is the key design criteria.

Kingman, AZ, and other wastewater reuse systems incorporate wetlands as a pretreatment for groundwater recharge. The results will potentially impact wastewater reuse scenarios, such as soil aquifer treatment (SAT) were water is ponded and allowed to infiltrate into the groundwater prior to groundwater recovery (Wilson *et al.*, 1995). Wetlands with long HRTs will tend to result in effluent, that serves as influent to the subsequent SAT process, with relatively high DOC, high SUVA levels, large fraction of refractory DOC and relatively high potential for forming disinfection by-products. These DOC characteristics may affect the removal of DOC by biodegradation and sorption during SAT.

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