Nature and Transformation of Dissolved Organic Matter in Treatment Wetlands

LARRY B. BARBER,*,[†]
JERRY A. LEENHEER,[‡]
TED I. NOYES,[‡] AND ERIC A. STILES[§]

U.S. Geological Survey, 3215 Marine Street, Boulder, Colorado 80303, U.S. Geological Survey, P.O. Box 25046, MS 408, Denver, Colorado 80225, and U.S. Bureau of Reclamation, P.O. Box 25007, D-8570, Denver, Colorado 80225

This investigation into the occurrence, character, and transformation of dissolved organic matter (DOM) in treatment wetlands in the western United States shows that (i) the nature of DOM in the source water has a major influence on transformations that occur during treatment, (ii) the climate factors have a secondary effect on transformations, (iii) the wetlands receiving treated wastewater can produce a net increase in DOM, and (iv) the hierarchical analytical approach used in this study can measure the subtle DOM transformations that occur. As wastewater treatment plant effluent passes through treatment wetlands, the DOM undergoes transformation to become more aromatic and oxygenated. Autochthonous sources are contributed to the DOM, the nature of which is governed by the developmental stage of the wetland system as well as vegetation patterns. Concentrations of specific wastewater-derived organic contaminants such as linear alkylbenzene sulfonate, caffeine, and ethylenediaminetetraacetic acid were significantly attenuated by wetland treatment and were not contributed by internal loading.

Introduction

Dissolved organic matter (DOM) plays a major role in biogeochemical processes in natural and treatment wetlands (*1*) and influences the transport characteristics, chemical interactions, and biological availability of trace elements and synthetic organic compounds (*2*). DOM consists of a continuum of macroscopic particles, biotic and abiotic colloids, dissolved macromolecules, and specific compounds (*3*). Wetlands are highly productive ecosystems, and DOM is simultaneously assimilated and produced; however, little is known about the chemical nature and fate of DOM in treatment wetlands (*4, 5*). Biological transformations can result in the formation of stable metabolites or complete degradation of specific components of the DOM (*6*).

Free water surface treatment wetlands consist of semi-aquatic emergent marshes that support a variety of biological, chemical, and physical functions and have been used to treat municipal, industrial, and agricultural effluents (*7–11*). Removal of contaminants by treatment wetlands is achieved by filtration/adsorption, volatilization, photolysis, and microbial transformations, the relative significance of each process being a function of chemical concentrations, environmental factors, and hydraulic retention time (HRT). A hierarchical analytical approach (*12–16*) is necessary for measuring the chemical characteristics of DOM when evaluating wetland transformations.

Four treatment wetlands in the western United States (Table 1) were selected to evaluate the effects of climate, wastewater characteristics, and operating conditions on the nature and fate of DOM. The focus of the study was analysis of water collected during synoptic samplings at the wetland sites. The analytical measurements provided data on the concentrations and molecular characteristics of the DOM and were used to monitor changes during wetland treatment.

Experimental Methods

Sampling. Sampling at each site involved field measurement of temperature, pH, specific conductance, and dissolved oxygen (DO). Water was collected for analysis of total organic carbon (TOC), dissolved (<0.45 μm) organic carbon (DOC), analytical scale DOC fractionation (DOC$_f$), DOC molecular weight (DOC$_{mw}$), ultraviolet light absorbance (UV$_{254}$), linear alkylbenzenesulfonate (LAS), caffeine, and ethylenediaminetetraacetic acid (EDTA). Large-volume samples ($\sim$20 L) were collected for preparative-scale DOM isolation (DOM$_p$) and characterization by Fourier transform infrared (FTIR) and ^{13}C nuclear magnetic resonance (^{13}C NMR) spectrometry. Samples for DOC, DOC$_f$, DOC$_{mw}$, and UV$_{254}$ analysis were filtered through 0.45-μm silver membranes and collected in amber glass bottles. Samples for LAS, EDTA, and caffeine were filtered through 1-μm glass fiber filters and preserved with 2% (v/v) formalin. Samples for DOM$_p$ were glass fiber filtered (0.3 μm), collected in polyethylene containers, and preserved with 0.5% (v/v) chloroform. All samples were stored at 4° C until analysis.

Analytical Methods. Detailed descriptions of the analytical methods and results are reported elsewhere (*17*). TOC and DOC were measured by heated persulfate oxidation with IR detection using a model 700 Oceanographic International carbon analyzer. Analytical-scale DOC$_f$ (*15, 16*) yields six fractions (Table 2) based on chromatographic characteristics at variable pH. Amberchrom GC71M (Supelco), a polymethacrylate polymer, was used as the hydrophobic sorbent. Bio-Rad (Hercules) AG-MP1 anion-exchange resin (OH$^-$ form) and AG-MP50 cation-exchange resin (H$^+$ form) were used for ion exchange. The sample was passed through the GC71M ($\sim$10 pore vol/min) at neutral pH to isolate the hydrophobic neutral (HPO$_n$) and hydrophobic base (HPO$_b$) fractions; the HPO$_b$ fraction was extracted with sulfuric acid, and the HPO$_n$ fraction was determined by the difference. Effluent from the GC71M column was acidified to pH 2 and passed through the resin again to isolate the hydrophobic acid (HPO$_a$) fraction. DOC that passed through the GC71M resin at pH 2 was fractionated into the hydrophilic base (HPI$_b$) fraction by cation exchange and the hydrophilic acid (HPI$_a$) fraction by anion exchange. Effluent from the ion-exchange resins was the hydrophilic neutral (HPI$_n$) fraction. DOC$_{mw}$ was determined by ultrafiltration (*18*) using a series of membranes (Amicon) with varying molecular weight cutoffs (100 000, 30 000, 10 000, 3000, 1000, and 500 Da). Absorbance was measured at 254 nm in a 1-cm quartz cell using a Bausch and Lomb Spectronics model 710 spectrometer.

LAS was measured by the method of Field et al. (*19*) using solid-phase extraction (SPE), injection-port derivatization gas chromatography/mass spectrometry (GC/MS). Octadecyl surface-modified silica (C$_{18}$) cartridges (Waters) were used

* Corresponding author phone: (303)541-3039; fax: (303)447-2505; e-mail: lbbarber@usgs.gov.
[†] U.S. Geological Survey, Boulder.
[‡] U.S. Geological Survey, Denver.
[§] U.S. Bureau of Reclamation.

TABLE 1. Characteristics of the Wetland Sites Investigated in This Study

San Jacinto, CA

multipurpose wetlands at Hemet/San Jacinto Regional Wastewater Reclamation Facility, located in
    southern California; operated by Eastern Municipal Water District; predominantly domestic sewage
    undergoes activated-sludge secondary treatment prior to discharge to the wetlands; system consists of two
    types of wetlands
        0.1-ha pilot cells (8 total): 4 1-phase cells (uniform emergent bulrush marsh) and 4 3-phase
          cells (marsh−pond−marsh); inflow to each cell, $\sim4.0 \times 10^4$ L/d; HRT, $\sim$13 d; inflow BOD,
          $\sim$10 mg/L
        10-ha integrated demonstration wetland: glove-shaped marsh consists of 5 fully vegetated (bulrush)
          inlet marsh treatment units ($\sim$40% of wetland area) that converge into open water/marsh habitat
          area ($\sim$20%), followed by 2 fully vegetated polishing marshs ($\sim$40%); effluent from polishing marshes
          is used or agriculture or recycled back through the WWTP plant; inflow (design), $\sim3.4 \times 10^6$ L/d;
          inflow (actual), $\sim9.5 \times 10^5$ L/d; HRT, 14 d; inflow BOD, $\sim$10 mg/L
        hot arid climate, newly established system (pilot cells $\sim$3 yr, demonstration wetland $\sim$1 yr)
August 1995 sampling (Table 3); collect samples from 1-phase cell influent (WWTP effluent) and effluent;
    3-phase cell influent (WWTP effluent), open water (midpoint), and effluent; demonstration wetland influent
    (WWTP effluent), open water zone (midpoint), and effluent

Arcata, CA

Arcata Marsh and Wildlife Sanctuary, located in northern California; 40-ha integrated wetland treatment
    system owned and operated by the city of Arcata, CA; predominantly domestic sewage undergoes solids removal
    and primary clarification prior to discharge to 2 ($\sim$22 ha total) aerated facultative lagoons in series; effluent
    from lagoons passes through 2 parallel fully vegetated bulrush treatment marshes ($\sim$6 ha, 90% plant cover),
    followed by 4 enhancement marshes in series ($\sim$12 ha, 20−40% plant cover); effluent from final enhancement
    marsh is discharged into Humboldt Bay; inflow, $\sim6.1 \times 10^6$ L/d; total system HRT, $\sim$50 d (30 d for lagoons,
    1 d for treatment marshes, 20 d for enhancement marshes); inflow BOD (lagoon effluent), 30−50 mg/L
        cool-wet maritime climate, mature system (>5 yr)
April 1995 sampling (Table 4); collect samples from primary clarifier (WWTP effluent); lagoon 1 effluent;
    lagoon 2 effluent; combined treatment marsh effluent; final enhancement marsh effluent

Halsey, OR

treatment wetlands at the Pope and Talbot non-chlorinated oxygen delignification Kraft pulp mill,
    located in western Oregon; operated by Oregon State University (OSU); secondary treated effluent is discharged
    into 10 pilot cells ($\sim$0.01 ha each) in paired configurations (subsurface flow rock bed, fully vegetated with cattail,
    fully vegetated with bulrush, open water) all run in parallel; effluent from treatment wetlands is discharged
    to Willamette River; inflow to each cell, $\sim6.5 \times 10^4 - 3.3 \times 10^5$ L/d; HRT, $\sim$2−10 d; inflow BOD, $\sim$25 mg/L
        cool-wet climate, immature system (<5 yr)
April 1995 sampling (Table 6); collect samples from pulp mill effluent, rock bed wetland effluent,
    open water wetland effluent, and fully vegetated bulrush wetland (10-d HRT) effluent

Corvallis, OR

Corvallis Dairy treatment wetland, located in western Oregon; operated by OSU; raw cow waste from facility
    washdown undergoes solids removal, is diluted with recycled wetland effluent, and is then discharged
    to 6 small ($\sim$0.02 ha) wetlands with alternating bulrush marsh and open water zones operated in series;
    wetland effluent is recycled through wetlands or used for irrigation; inflow of diluted dairy effluent,
    $\sim5.3 \times 10^3$ L/d; HRT, $\sim$7 d; inflow BOD, $\sim$560 mg/L
        cool-wet climate, immature system (<5 yr)
April 1995 sampling (Table 7); collect samples from dairy effluent after solids removal but
    prior to dilution and final treatment wetland effluent

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to extract 1-L samples after ionic strength adjustment with sodium chloride. The C_{18} was eluted with 0.1 m tetrabutylammonium hydrogen sulfate in chloroform, and the extracts were analyzed by GC/MS (Hewlett-Packard 5890 GC/5970 MSD) in the full-scan and selected-ion monitoring modes. EDTA was measured using a modification (*20*) of the method of Schaffner and Giger (*21*). Samples were evaporated to dryness, acidified with formic acid:distilled water (50:50), and evaporated to dryness again. Acetyl chloride:propanol (10:90) was added, the sample was heated at 85° C for 1 h, and the esters were extracted into chloroform. The extracts were evaporated, dissolved in toluene, and analyzed by GC/MS. Caffeine was determined by C_{18} isolation, elution with ethyl acetate, and GC/MS analysis.

The DOM_p procedure (*22*) isolated milligram quantities of fractions similar to those analytically determined by DOC_f and uses the same notation (Table 2). The isolation involves vacuum evaporation of 20-L samples to 500 mL with no pH adjustment. Carbonates, organic colloids, humic acids, silica, and metal oxyhydroxides precipitated during evaporation. The carbonates and oxyhydroxides were dissolved with hydrochloric acid; the organic colloids, humic acids, and silica were separated by centrifugation. Organic colloids and humic acids were dispersed with sodium hydroxide, and the

sample was filtered to remove silica. Organic colloids and humic acids were then precipitated with hydrochloric acid, centrifuged, and freeze-dried. The sample concentrate was adjusted to pH 1 and passed through columns of XAD-8 and XAD-4 (Rohm and Hass) macroreticular resins in series. The HPO_a fraction was desorbed from the XAD-8 column with 0.1 N sodium hydroxide followed by elution of the combined hydrophobic neutral and base (HPO_{n+b}) fraction with acetonitrile:water (75:25). The XAD-4 column was desorbed with acetonitrile:water to give a combined hydrophilic acid and base (HPI_{a+b}) fraction. Effluent from the XAD-4 was vacuum evaporated and passed through columns of cation- and anion-exchange resin in series. Effluent from the ion-exchange columns is the HPI_n fraction. DOM on the anion-exchange resin was the ultrahydrophilic acid ($UHPI_a$) fraction and was desorbed with sodium hydroxide, methylated with acetyl chloride:methanol (5:95), and purified on XAD-8. The DOM_p fractions were freeze-dried, and the mass of isolated material was determined gravimetrically. Elemental analysis of select DOM_p fractions was performed as described in Huffman and Stuber (*23*).

FTIR analysis of select DOM_p fractions was performed on $\sim$10 mg of residue dispersed in potassium bromide pellets using a Perkin-Elmer System 2000 FTIR spectrometer. Solid-

TABLE 2. Summary of Fractions Produced by DOC$_f$ and DOM$_p$ Analysis (*15, 16, 22*), and FTIR Bands and ^{13}C NMR Chemical Shifts for Important Functional Groups That Are Characteristic of Natural Organic Matter (*34*)

		DOC$_f$ and DOMp	
fraction	abbreviation	organic compound class	
hydrophobic acid	HPO$_a$	C$_5$–C$_9$ aliphatic carboxylic acids; 1- and 2-ring aromatic carboxylic acids; 1- and 2-ring phenols; fulvic acid; linear alkylbenzene sulfonate (LAS), LAS degradation products	
hydrophobic base	HPO$_b$	1- and 2-ring aromatic amines except pyridine; proteinaceous substances; cationic surfactants	
hydrophobic neutral	HPO$_n$	hydrocarbons; >C$_5$ aliphatic alcohols, amides, esters, ketones, and aldehydes; >C$_9$ aliphatic carboxylic acids and amines; >3-ring aromatic carboxylic acids and amines; chlorophyll and related pigments; LAS and optical brighteners	
hydrophilic acid	HPI$_a$	<C$_5$ aliphatic carboxylic acids; polyfunctional carboxylic acids; LAS degradation products	
hydrophilic base	HPI$_b$	<C$_9$ aliphatic amines; pyridine; amino acids	
hydrophilic neutral	HPI$_n$	<C$_5$ aliphatic amides, alcohols, aldehydes, esters, and ketones; polyfunctional alcohols; carbohydrates; cyclic amides	

		FTIR	
wavenumber (cm^{-1})	bond	functional group	typical compounds in DOM fractions
1000–1050	SO	sulfonic acids	LAS and LAS degradation products, sulfonated lignins
1000–1150	CO	alcohols and ethers	carbohydrates
1150–1250	COOH	carboxylates and esters	aliphatic and aromatic acids, fulvic and humic acid, amino acids
1440	CCH$_3$	methyl ester	methylated acids
1550	CONHR	amide 2, secondary amides	peptides
1670	CONHR	amide 1, primary and secondary amides	peptides, *N*-acetyl amino sugars
1680–1800	COOH, COOR, RCOH	carboxylates, esters, ketones	aliphatic and aromatic acids, fulvic and humic acid, amino acids
2800–3000	CH	hydrocarbons	petroleum products, lipids
2500–3600	OH NH	alcohols, phenols, carboxylates, amides	carbohydrates, humic and fulvic acid, proteins

		^{13}C NMR	
chemical shift (ppm)	bond	class	typical compounds in DOM fractions
0–50	CC or CH	aliphatic-1	aliphatic hydrocarbons
45–55	CN	aliphatic-2	proteins
60–90	CO	aliphatic-3	alcohols, esters, ethers, carbohydrates
90–110	OCO	anomeric	carbohydrates, sugars
100–160	ϕ	aromatic	petroleum, humics
100–130	ϕ	aromatic-1	
120–140	ϕ-C	aromatic-2	alkyl benzenes
140–160	ϕ-OH	aromatic-3	phenols, humics, lignins
145	ϕ-SO$_3$	aromatic sulfonate	sulfonated surfactants
160–190	COOH, COOR, CONHR	carboxylate, ester, amide	organic acids, humics, proteins
190–220	COH, RCOR	ketones, aldehydes	humics

state cross-polarization magic angle spinning ^{13}C NMR analysis was performed on 10–300 mg of material using a 200 MHz Chemagnetics CMX spectrometer with a 7.5-mm diameter probe and spinning rate of 4000 Hz. Table 2 summarizes FTIR and ^{13}C NMR characteristics for important functional groups in natural and sewage-derived DOM.

Results

San Jacinto, California. The San Jacinto wetlands (Table 1) receive municipal wastewater treatment plant (WWTP) effluent (*9, 24, 25*) and were sampled during March 1994 and August 1995. Select results for August 1995 are summarized in Table 3, and a detailed compilation of all data is presented elsewhere (*17*). Concentrations of DOC in the 1- and 3-phase pilot cells increased 74% and 100% between the wetland inflow and outflow. The open water in the 3-phase cell had high particulate organic carbon (POC) as the result of algae growth, most of which was removed by the outlet marsh. UV$_{254}$ is an indirect measure of aromaticity and an indicator of vascular plant-derived DOM (*3, 26*). Specific absorbance (SA$_{254}$ = UV$_{254}$/DOC) decreased 13% in the 3-phase cells, indicating DOC input from algal sources, which have lower molar absorptivity than vascular plant-derived DOC (*27*). In

contrast, the fully vegetated 1-phase cells had a 60% increase in SA$_{254}$, indicating DOC contributions from the dense bulrush vegetation. DOC$_f$ results for the pilot cells indicated that the WWTP effluent was predominantly HPO$_a$ and HPI$_a$ with a significant HPO$_n$ and HPI$_b$ component. Effluent from the 1-phase cell had an increase in the HPO$_a$ fraction (plant-derived humic substances) and a decrease in the HPO$_n$, HPI$_a$, and HPI$_b$ fractions. The main difference between the inflow and outflow in the 3-phase cells was a decrease in the HPO$_n$ fraction and an increase in the HPO$_a$ and HPI$_a$ fractions. Concentrations of LAS ranged from 2 to 9 μg/L, and there was no clear trend of removal in the pilot cells. EDTA concentrations in the WWTP effluent were an order of magnitude greater than LAS, and concentrations were attenuated 48% and 59% in the 1- and 3-phase cells. Caffeine concentrations in the WWTP effluent were less than 1 μg/L and were slightly reduced in both 1- and 3-phase cells.

During August 1995, the demonstration wetland had an HRT >14 d due to low hydraulic loading and high evapotranspiration (ET) rates, and there was no discharge at the wetland outflow (water was nearly stagnant). The concentrating effect of ET was evident from the 73% increase in specific conductance. In contrast, there was a 226% increase

TABLE 3. Data for the San Jacinto, CA, Wetland Site, August 1995[a]

site	SC (μS/cm)	DO (mg/L)	TOC (mg/L)	DOC (mg/L)	UV$_{254}$ (cm)	SA$_{254}$ (L mg^{-1} m^{-1})	LAS (μg/L)	EDTA (μg/L)	caffeine (μg/L)
1-phase WWTP effluent	982	0.3	9.7	8.9	0.129	15	4.8	92.0	0.3
1-phase wetland effluent	975	0.3	14.7	15.5	0.365	24	9.1	47.5	0.2
3-phase WWTP effluent	977	0.2	8.6	8.5	0.134	16	1.5	71.2	0.3
3-phase wetland midpoint	981	0.3	33.1	14.9	0.235	16	9.2	43.3	0.3
3-phase wetland effluent	1031	0.1	16.4	17.0	0.236	14	2.5	29.0	0.1
demonstration WWTP effluent	849	3.6	9.7	8.9	0.140	16	6.2	78.6	0.9
demonstration wetland midpoint	1433	3.9	23.3	20.4	0.245	12		78.3	
demonstration wetland effluent[b]	1469	11.5	32.2	29.0	0.251	9	4.0	70.9	0.1

	1-phase WWTP effluent	1-phase wetland effluent	3-phase WWTP effluent	3-phase wetland midpoint	3-phase wetland effluent	demon-stration WWTP effluent	demon-stration wetland midpoint	demon-stration wetland effluent
				DOC$_f$ Analysis				
HPO$_a$ (%)	33	46	36	44	39	41	39	35
HPO$_b$ (%)	1	<1	1	1	1	1	1	1
HPO$_n$ (%)	20	18	12	11	5	8	5	1
HPI$_a$ (%)	27	15	30	26	37	36	37	44
HPI$_b$ (%)	18	13	17	16	16	12	16	19
HPI$_n$ (%)	2	7	5	2	2	1	2	1
				DOM$_p$ Analysis				
total DOM (mg)[c]	–	–	–	–	–	211	348	463
DOC (mg/L)[d]	–	–	–	–	–	4.8	9.1	10.6
HPO$_a$ (%)	–	–	–	–	–	39	48	45
HPO$_{n+b}$ (%)	–	–	–	–	–	13	10	7
HPI$_{a+b}$ (%)	–	–	–	–	–	42	34	46
UHPI$_a$ (%)	–	–	–	–	–	–	–	–
HPI$_n$ (%)	–	–	–	–	–	7	8	2
colloid (%)[e]	–	–	–	–	–	–	262	–

[a] WWTP effluent, wastewater treatment plant effluent inflow to wetlands; SC, specific conductance; DO, dissolved oxygen; TOC, total organic carbon; DOC, dissolved organic carbon; UV$_{254}$, absorbance at 254 nm; SA$_{254}$, specific absorbance at 254 nm; LAS, linear alkylbenzenesulfonates; EDTA, ethylenediaminetetraacetic acid; HPO$_a$, hydrophobic acid; HPO$_b$, hydrophobic base; HPO$_n$, hydrophobic neutral; HPI$_a$, hydrophilic acid; HPI$_b$, hydrophilic base; HPI$_n$, hydrophilic neutral; UHPI$_a$, ultrahydrophilic acid; –, not analyzed. [b] Outflow was not discharging due to long hydraulic retention time and high evapotranspiration. Sample from very low flow, nearly stagnant water. [c] Total mass of DOM fractions isolated from approximately 20-L sample. [d] DOC determined by multiplying mg/L DOM × 0.5. [e] Colloid fraction is not "dissolved" and thus not included when summing DOM fractions. Colloid (%) is calculated relative to total DOM.

in DOC, indicating internal loading from autochthonous organic matter. SA$_{254}$ decreased 53% across the wetland, indicating that DOC at the outlet was less aromatic in character than the WWTP inflow as was observed in the 3-phase pilot cells. These results are consistent with an intense algae bloom occurring in the open water areas at the time of sampling due to the release of nutrients from the soil in the recently flooded demonstration wetland (∼1 yr). Because of the early stage of the growth curve (25), there was only about 30% emergent vegetation coverage and little biomass accumulation. DOC$_f$ analysis indicated a decrease in the HPO$_a$ fraction and an increase in the HPI$_a$ and HPI$_b$ fractions between the WWTP and demonstration wetland effluents. DOM$_p$ results were in agreement with the DOC$_f$ data, and yielded primarily the HPO$_a$ and HPI$_{a+b}$ fractions. The DOC$_f$ data had close mass balance with DOC and thus are best for describing distributions of the various fractions and making comparisons within and between sites. DOM$_p$ mass balance relative to DOC was low and variable (37–54%) because of incomplete recovery of the colloid fraction (increases to >80% mass balance when the colloid fraction is included) and loss of volatile components such as fatty acids. The DOM$_p$ fractions are more qualitative than for DOC$_f$, but provide valuable insight into DOM molecular characteristics when subjected to spectroscopic analysis.

FTIR analysis (Figure 1A) of the WWTP effluent DOM$_p$ HPO$_a$ and HPO$_{n+b}$ fractions were similar, and both were characterized by hydrocarbon (2920 cm^{-1}) and carboxylic acid (1720 and 1200 cm^{-1}) components (Table 2), with the HPO$_a$ fraction having greater carboxylate and the HPO$_{n+b}$ fraction having greater hydrocarbon content. Of particular interest is the small peak around 1050 cm^{-1}, indicating LAS related aromatic sulfonate compounds. The HPI$_{a+b}$ fraction was characterized by hydroxy (3402 cm^{-1}) and amide-1 (1670 cm^{-1}) peaks. After wetland treatment, both the HPO$_a$ and the HPO$_{n+b}$ fractions showed reduction in hydrocarbon and aromatic sulfonate content (attenuation of LAS also was observed), and the relative intensity of the amide-1 peak in the HPI$_{a+b}$ fraction decreased. There was broadening of the FTIR bands during wetland treatment, indicating that the DOM becomes more complex as degradation progresses.

^{13}C NMR analysis of the WWTP effluent HPO$_a$ and HPO$_{n+b}$ fractions (Figure 1B) indicated enrichment in aliphatic-1 (0–50 ppm) and aromatic (100–160 ppm) carbon, with only minor aliphatic-2 (45–55 ppm) and aliphatic-3 (60–90 ppm) carbon (Table 2). The main difference between the fractions is enrichment in the carboxylate–ester–amide (CEA) carbon (160–190 ppm) in the HPO$_a$ fraction and depletion in aromatic carbon in the HPO$_{n+b}$ fraction. The HPI$_{a+b}$ fraction was enriched in aliphatic-3 and CEA carbon. The wetland effluent HPO$_a$ fraction decreased in aromatic carbon, consistent with the SA$_{254}$ data, which indicates that the increased carbon content in the wetland is algal derived. The HPO$_{n+b}$ fraction in the wetland effluent indicated little change, and the HPI$_{a+b}$ increased in CEA and anomeric (90–110 ppm) carbon relative to the WWTP effluent.

Arcata, California. The Arcata wetlands (Table 1) receive WWTP effluent from the city of Arcata, CA (9, 28), and were
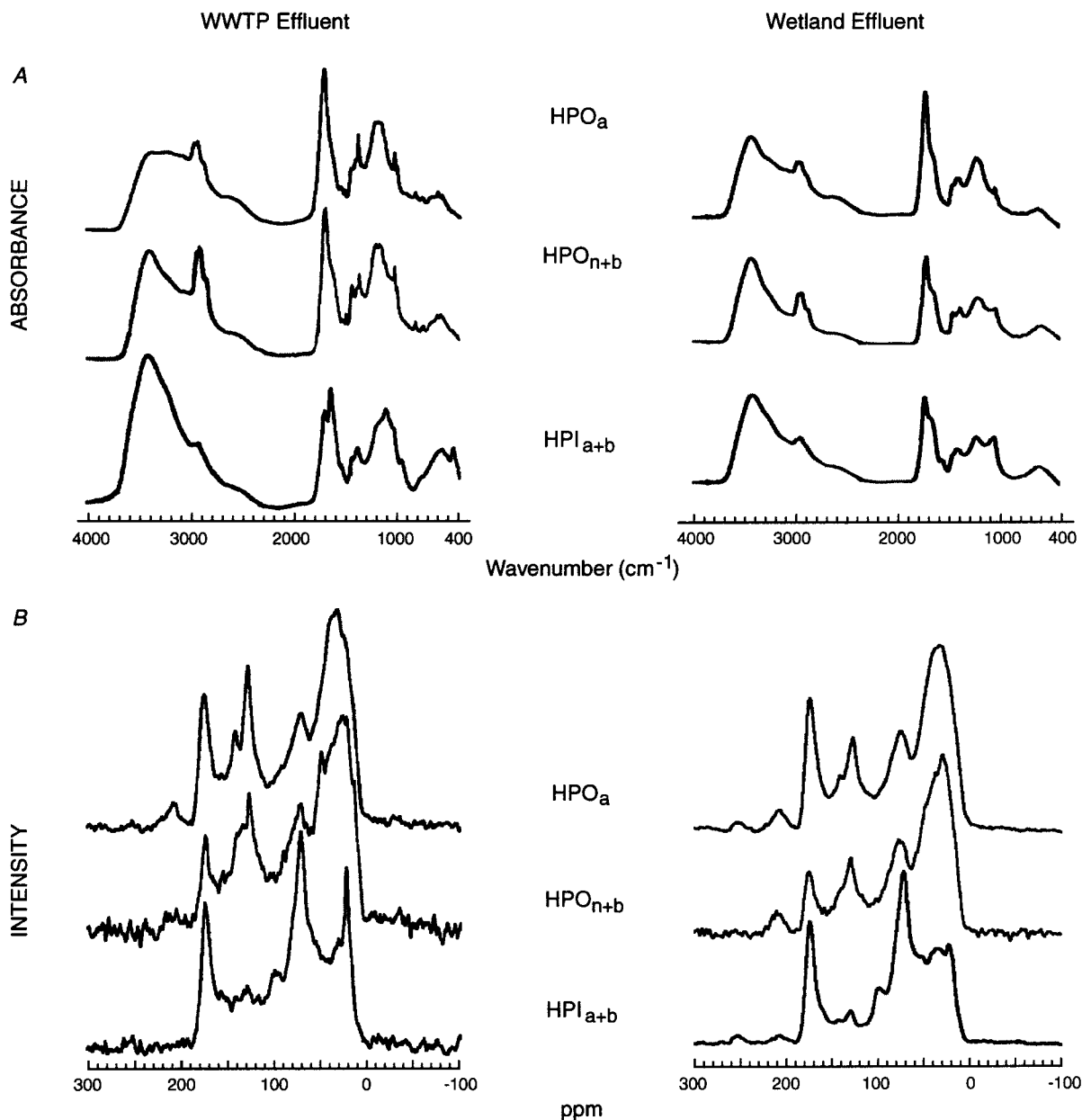
WWTP Effluent

Wetland Effluent

FIGURE 1. FTIR (A) and ^{13}C NMR (B) spectra for select DOM_p fractions from the San Jacinto, CA, Demonstration Treatment Wetlands (Table 1) collected during August 1995.

sampled during July 1994 and April 1995. Select results for April 1995 are summarized in Table 4, and all data are presented elsewhere (17). DOC decreased 61% across the two facultative lagoons and then remained relatively constant throughout the rest of the treatment system. SA_{254} increased across the wetlands, indicating that the DOC becomes more aromatic due to selective removal of aliphatic DOM and input of vascular plant-derived DOM. From 57 to 71% of the DOC in the WWTP effluent was <30 000 Da and 21−50% was <3000 Da; there was a decrease in DOC_{mw} during wetland treatment. Concentrations of LAS decreased 99% in the first lagoon, but low levels persisted throughout the rest of the wetlands. EDTA concentrations in the WWTP effluent were similar to LAS, but only 63% of the EDTA was removed in the first lagoon; however, 98% of the EDTA was removed in the final wetland effluent. Caffeine in the WWTP effluent was about 50% of the LAS and EDTA values, and as was the case for LAS, 99% was removed in the first lagoon.

DOC_f analysis indicated that the WWTP effluent was enriched in HPO_a with significant HPO_n, HPI_a, HPI_b, and HPI_n fractions. There was a shift in the HPO/HPI ratio between the WWTP effluent and the second lagoon, with the DOC becoming more hydrophilic due to decreasing HPO_a and HPO_n and increasing HPI_a and HPI_b content. The HPO_a fraction increased in the treatment and enhancement marshes following the initial decrease in the lagoons. DOM_p analysis of the WWTP effluent consisted predominantly of HPO_a with lesser amounts of the HPI_{a+b} and HPI_n fractions. There also was a significant colloid fraction.

Elemental analysis (Table 5) of the WWTP effluent HPO_a fraction yielded 50% carbon whereas the colloid fraction was only 38% carbon due to high ash content. On an ash-free basis, the HPO_a fraction was 54% and the colloid fraction was 56% carbon. The colloid fraction was enriched in nitrogen and depleted in oxygen and hydrogen relative to the HPO_a fraction. The wetland effluent HPO_a fraction was enriched in oxygen and depleted in carbon, nitrogen, and hydrogen relative to the WWTP effluent HPO_a fraction. The atomic hydrogen/carbon ratio (H/C), another indicator of aromaticity, was higher (more aliphatic) in the colloid fraction than

TABLE 4. Data for the Arcata, CA, Wetland Site, April 1995[a]

site	SC (μS/cm)	DO (mg/L)	TOC (mg/L)	DOC (mg/L)	UV$_{254}$ (cm)	SA$_{254}$ (L mg^{-1} m^{-1})	DOC$_{mw}$ <100 000 Da (%)	<30 000 Da (%)	<10 000 Da (%)	<3000 Da (%)	<1000 Da (%)	LAS (μg/L)	EDTA (μg/L)	caffeine (μg/L)
WWTP effluent	400	1.0	37.8	27.4	0.316	12	56	57	43	37	29	119	100	45.1
lagoon 1 effluent	352	7.8	17.7	12.5	0.199	16	70	63	62	21	27	1.3	36.8	0.5
lagoon 2 effluent	312	9.4	18.3	12.8	0.200	16	70	60	50	36	38	0.5	22.9	<0.1
treatment marsh effluent	440	0.1	16.5	11.0	0.155	14	77	69	58	50	28	<0.1	20.0	<0.1
enhancement marsh effluent	321	1.4	10.3	12.4	0.251	20	75	71	55	38	26	1.9	1.6	<0.1

	WWTP effluent	lagoon 1 effluent	lagoon 2 effluent	treatment marsh effluent	enhancement marsh effluent
			DOC$_f$ Analysis		
HPO$_a$ (%)	43	32	26	33	43
HPO$_b$ (%)	2	1	1	2	2
HPO$_n$ (%)	17	4	7	9	5
HPI$_a$ (%)	15	27	39	14	10
HPI$_b$ (%)	10	21	20	20	21
HPI$_n$ (%)	14	16	7	24	20
			DOM$_p$ Analysis		
total DOM (mg)[b]	392	392	187	180	185
DOC (mg/L)[c]	11.2	10.9	5.6	4.7	5.1
HPO$_a$ (%)	46	63	56	45	56
HPO$_{n+b}$ (%)	—	—	—	15	15
HPI$_{a+b}$ (%)	30	21	24	26	20
UHPI$_a$ (%)	5	4	9	4	5
HPI$_n$ (%)	19	12	11	10	4
colloid (%)[d]	124	83	22	240	44

[a] See Table 3 for explanation of abbreviations. [b] Total mass of DOM fractions isolated from approximately 20-L sample. [c] DOC determined by multiplying mg/L DOM × 0.5. [d] Colloid fraction is not "dissolved" and thus not included when summing DOM fractions. Colloid (%) is calculated relative to total DOM.

TABLE 5. Elemental Analysis of Select DOM$_p$ Fractions from the Arcata, CA; Halsey, OR; and Corvallis, OR, Wetland Sites[a]

element	Arcata WWTP effluent colloid	Arcata WWTP effluent HPO$_a$	Arcata enhancement marsh effluent HPO$_a$	Halsey vegetated wetland effluent colloid	Halsey vegetated wetland effluent HPO$_a$, pH 5	Halsey vegetated wetland effluent HPO$_a$, pH 0	Corvallis wetland effluent colloid	Corvallis wetland effluent HPO$_a$
carbon (%)	37.9	49.8	50.1	34.1	47.5	31.3	38.7	54.7
hydrogen (%)	6.3	6.1	5.3	3.7	4.3	3.4	5.9	5.9
oxygen (%)	19.9	31.0	39.5	22.9	36.0	39.5	19.3	35.6
nitrogen (%)	3.3	3.8	2.8	1.0	0.4	0.5	4.6	2.7
ash (%)	32.5	8.1	2.6	34.4	3.1	22.1	26.0	1.4
sulfur (%)	—	—	—	—	4.3	4.9	—	—
chlorine (%)	—	—	—	—	9.6	14.5	—	—
atomic H/C	1.98	1.46	1.34	1.29	1.09	1.26	1.81	1.29
atomic O/C	0.39	0.47	0.59	0.50	0.56	0.95	0.39	0.48
				Ash Free				
carbon (%)	56.1	54.2	51.4	51.9	49.0	40.2	52.4	55.5
hydrogen (%)	9.3	6.6	5.8	5.6	4.4	4.3	7.9	6.0
oxygen (%)	29.5	33.8	40.5	34.8	37.1	50.7	26.1	36.1
nitrogen (%)	4.8	4.1	2.9	1.6	0.4	0.6	6.2	2.7
sulfur (%)	—	—	—	—	4.6	6.3	—	—
chlorine (%)	—	—	—	—	9.9	18.6	—	—

[a] WWTP effluent, wastewater treatment plant effluent inflow to wetlands; HPO$_a$, hydrophobic acid; —, not analyzed.

the HPO$_a$ fraction and decreased between the WWTP and wetland effluents. These results are consistent with the colloids having a significant lipid content and indicate that DOM produced in the wetland is more aromatic than wastewater DOM. The atomic oxygen/carbon ratio (O/C) was greater for the HPO$_a$ fraction than the colloid fraction and increased between the WWTP and wetland effluents, indicating that DOM is enriched in oxygen by wetland processes.

FTIR analysis (Figure 2A) shows that the WWTP effluent colloid fraction was enriched in amide-1, hydrocarbon, and carbohydrate (1150−1000 cm^{-1}) functional groups, indicating bacteria-derived glycoprotein material. The HPO$_a$ fraction contained hydrocarbon, carboxylate, and aromatic sulfonate peaks; the HPI$_{a+b}$ fraction contained carboxylate, amide-1, and amide-2 (1550 cm^{-1}) peaks; and the HPI$_n$ fraction was enriched in amide-1 and CO (carbohydrate) content (1100 cm^{-1}). The wetland effluent colloid fraction had a significant
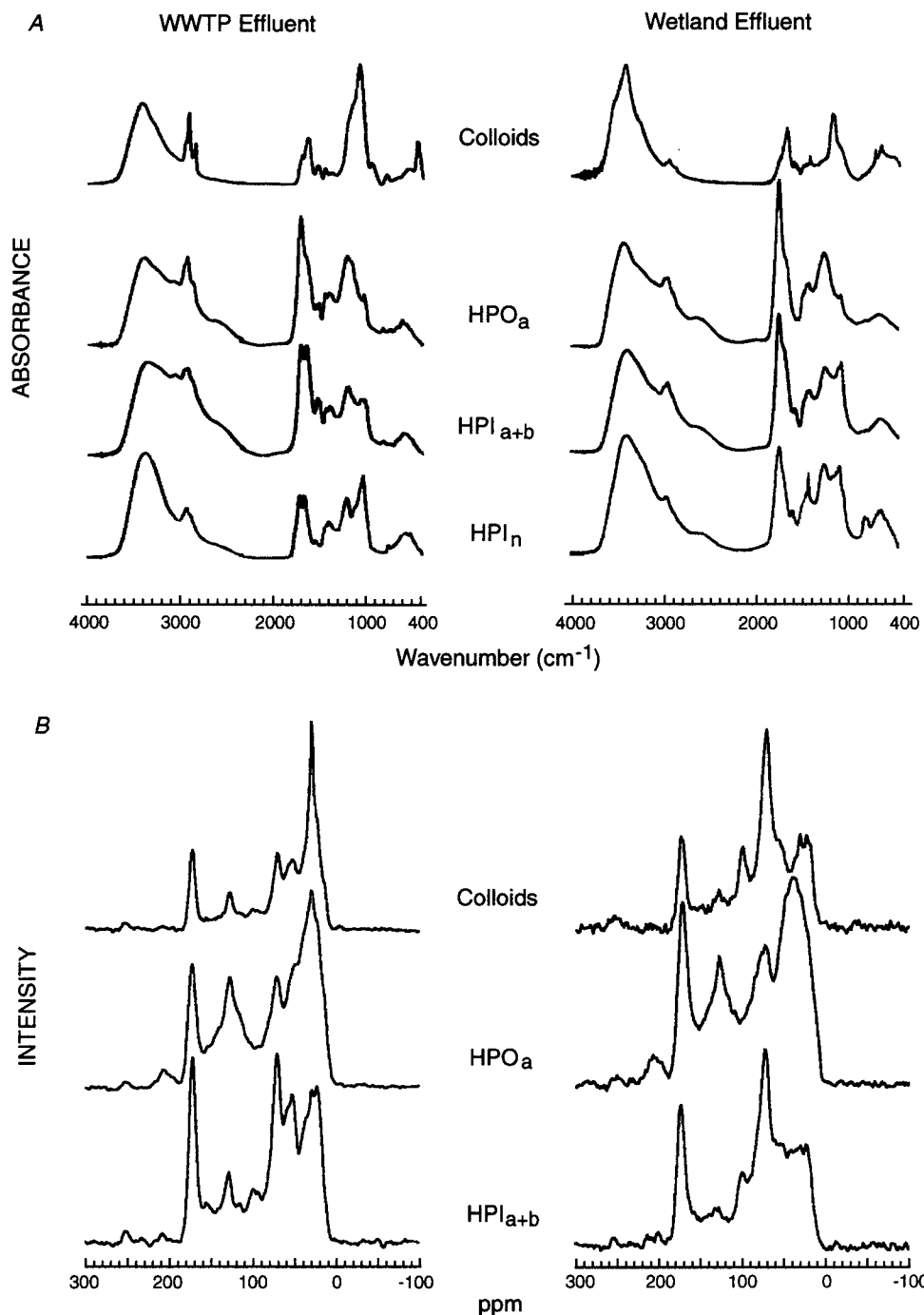
FIGURE 2. FTIR (A) and ^{13}C NMR (B) spectra for select DOM$_p$ fractions from the Arcata, CA, Treatment Wetlands (Table 1) collected during April 1995.

decrease in the hydrocarbon and carbohydrate components. Although similar to the WWTP effluent, the wetland effluent HPO$_a$ fraction had decreased hydrocarbon and aromatic sulfonate content and increased carboxylate content. The wetland effluent HPI$_{a+b}$ and HPI$_n$ fractions decreased in hydrocarbon and amide content and increased in carboxylate content relative to the WWTP effluent.

^{13}C NMR analysis (Figure 2B) of the WWTP effluent colloid fraction was dominated by aliphatic-1 with lesser amounts of aliphatic-2, aliphatic-3, aromatic, and CEA carbon, indicating relatively undegraded organic matter such as lipids and sugars. The HPO$_a$ fraction was enriched in CEA and aromatic carbon relative to the colloid fraction, and the HPI$_{a+b}$ fraction was enriched in aliphatic-2, aliphatic-3, CEA, and anomeric carbon. The wetland effluent colloid fraction was enriched in aliphatic-3 and depleted in aliphatic-1 carbon; the HPO$_a$ fraction was enriched in CEA carbon; and the HPI$_{a+b}$ fraction was enriched in aliphatic-3 and anomeric carbon relative to the WWTP effluent, indicating enrichment in oxygen containing functional groups during wetland treatment.

Halsey, Oregon. The Halsey wetlands (Table 1) receive secondary treated pulp mill effluent (29). Select results for the April 1995 sampling are summarized in Table 6, and all data are presented elsewhere (17). DOC in the pulp mill effluent was 299 mg/L, and concentrations decreased 18—31% in effluents from the various wetland configurations. The pulp mill effluent was highly colored as indicated by the large UV$_{254}$ and SA$_{254}$ values. DOC$_{mw}$ analysis indicated that, except for the rock bed wetland, ~85% of the DOC had a

TABLE 6. Data for the Halsey, OR, Wetland Site, April 1995[a]

site	SC (μS/cm)	DO (mg/L)	TOC (mg/L)	DOC (mg/L)	UV$_{254}$ (cm)	SA$_{254}$ (L mg^{-1} m^{-1})	DOC$_{mw}$ <100 000 Da (%)	<30 000 Da (%)	<10 000 Da (%)	<3000 Da (%)	<1000 Da (%)	LAS (μg/L)	EDTA (μg/L)	caffeine (μg/L)
pulp mill effluent	3220	0.1	299	299	8.22	28	94	85	28	18	19	10.0	—	<0.1
rock bed wetland effluent	3370	0.1	259	244	7.56	31	44	40	34	29	23	11.2	—	<0.1
open water wetland effluent	3300	0.2	284	222	6.40	29	92	85	30	23	17	3.4	—	<0.1
vegetated wetland effluent	3290	0.1	243	206	6.12	30	94	86	64	16	18	7.9	—	<0.1

	pulp mill effluent	rock bed wetland effluent	open water wetland effluent	vegetated wetland effluent
		DOC$_f$ Analysis		
HPO$_a$ (%)	53	54	53	60
HPO$_b$ (%)	2	2	2	<1
HPO$_n$ (%)	11	9	7	<1
HPI$_a$ (%)	28	27	30	34
HPI$_b$ (%)	6	8	8	6
HPI$_n$ (%)	<1	<1	<1	<1
		DOM$_p$ Analysis		
total DOM (mg)[b]	5481	—	—	6211
DOC (mg/L)[c]	138	—	—	162
HPO$_a$, pH 5 (%)	15	—	—	52[d]
HPO$_a$, pH 2 (%)	48	—	—	26[e]
HPO$_a$, pH 0 (%)	18	—	—	4
HPO$_n$ (%)	5	—	—	15
HPI$_a$ (%)	6	—	—	2
UHPI$_a$ (%)	4	—	—	1[f]
HPI$_n$ (%)	4	—	—	—
colloid (%)[g]	93	—	—	13

[a] See Table 3 for explanation of abbreviations. [b] Total mass of DOM fractions isolated from approximately 20-L sample. [c] DOC determined by multiplying mg/L DOM × 0.5. [d] HPO$_a$, pH 4. [e] HPO$_a$, pH 1. [f] Combined UHPI$_a$ and HPI$_n$ fractions. [g] Colloid fraction is not "dissolved" and thus not included when summing DOM fractions. Colloid (%) is calculated relative to total DOM.

molecular weight <30 000 Da but only 16−23% was <3000 Da. There were low concentrations of LAS in the pulp mill effluent with 66% and 21% reductions in the open water and fully vegetated wetlands and a slight increase in the rock bed wetland. No caffeine was detected, and EDTA was not analyzed. DOC$_f$ analysis of the pulp mill effluent was dominated by the HPO$_a$ fraction with lesser amounts of the HPI$_a$ and HPO$_n$ fractions. The open water and fully vegetated wetland effluents had increased HPI$_a$ and decreased HPO$_n$ fractions, and the fully vegetated wetland had increased HPO$_a$. There was little change in the rock bed effluent. Because of the complexity of the pulp mill effluent, the DOM$_p$ procedure was modified to further fractionate the HPO$_a$ fraction by pH gradient (pH 5, 2, and 0). DOM$_p$ data indicated that the pulp mill and wetland effluents were dominated by the HPO$_a$ fractions. There was a large colloid fraction in the pulp mill effluent, which decreased in the wetlands.

Elemental analysis (Table 5) indicates that the wetland effluent colloid and HPO$_a$ fractions had lower carbon, hydrogen, and nitrogen content than WWTP wetland effluents. The DOM also contained a significant amount of chlorine and sulfur. The H/C and O/C ratios of the HPO$_a$ fractions indicate that the DOM is more aromatic and oxygenated than DOM in WWTP effluent and varied as a function of pH. At both pH 5 and 0, the HPO$_a$ fraction had low H/C ratios, relative to WWTP effluent, indicating the aromatic nature of the DOM. At pH 0, the HPO$_a$ was depleted in carbon and enriched in oxygen relative to pH 5 and was less aromatic.

In contrast to colloids isolated from WWTP effluents, which were primarily bacterial biomass, the FTIR spectra (Figure 3A) of the pulp mill effluent colloids were more "humic

like", indicating that they were primarily precipitated humic acids, although there was a significant amide-1 peak. The HPO$_a$ pH = 0, HPO$_{n+b}$, and HPI$_{a+b}$ fractions contained significant aromatic sulfonate peaks, indicating the presence of sulfonated lignin compounds. The HPI$_{a+b}$ fraction was enriched in oxygen functional groups (1720 and 1100 cm^{-1}) relative to the HPO$_a$ pH = 0 and HPO$_{n+b}$ fractions. There was little change in the FTIR character of the DOM in the wetland effluents, with the most notable difference being broadening of the peaks.

The pulp mill effluent colloid fraction was very aromatic as shown by the ^{13}C NMR spectra (Figure 3B), reflecting the lignin-rich character of the source water. The HPO$_a$ pH = 0 and HPI$_{a+b}$ fractions were enriched in CEA and aliphatic-2 carbon relative to the colloid and HPO$_{n+b}$ fractions. There were significant differences in the ^{13}C NMR spectra of the HPO$_a$ fractions isolated at pH 5 and pH 0; at pH 5, the HPO$_a$ fraction was very aromatic and similar to the HPO$_{n+b}$ fraction whereas at pH 0 the HPO$_a$ fraction was highly depleted in aromatic content and similar to the HPI$_{a+b}$ fraction. After wetland treatment, the CEA component increased in the colloid fraction, the aromatic content increased in the HPO$_{n+b}$ fraction, and the HPO$_a$ pH = 0 and HPI$_{a+b}$ fractions had little change.

Corvallis, Oregon. The Corvallis wetlands (Table 1) receive wastewater from the Oregon State University dairy unit (30). Samples were collected in April 1995 from the dairy parlor and the wetland effluents (Table 7), and all data are presented elsewhere (17). Specific conductance of the dairy effluent was 9820 μS/cm and decreased by 95% in the wetland effluent, indicating significant dilution with low conductivity water. TOC in the dairy effluent was very high due to the large POC
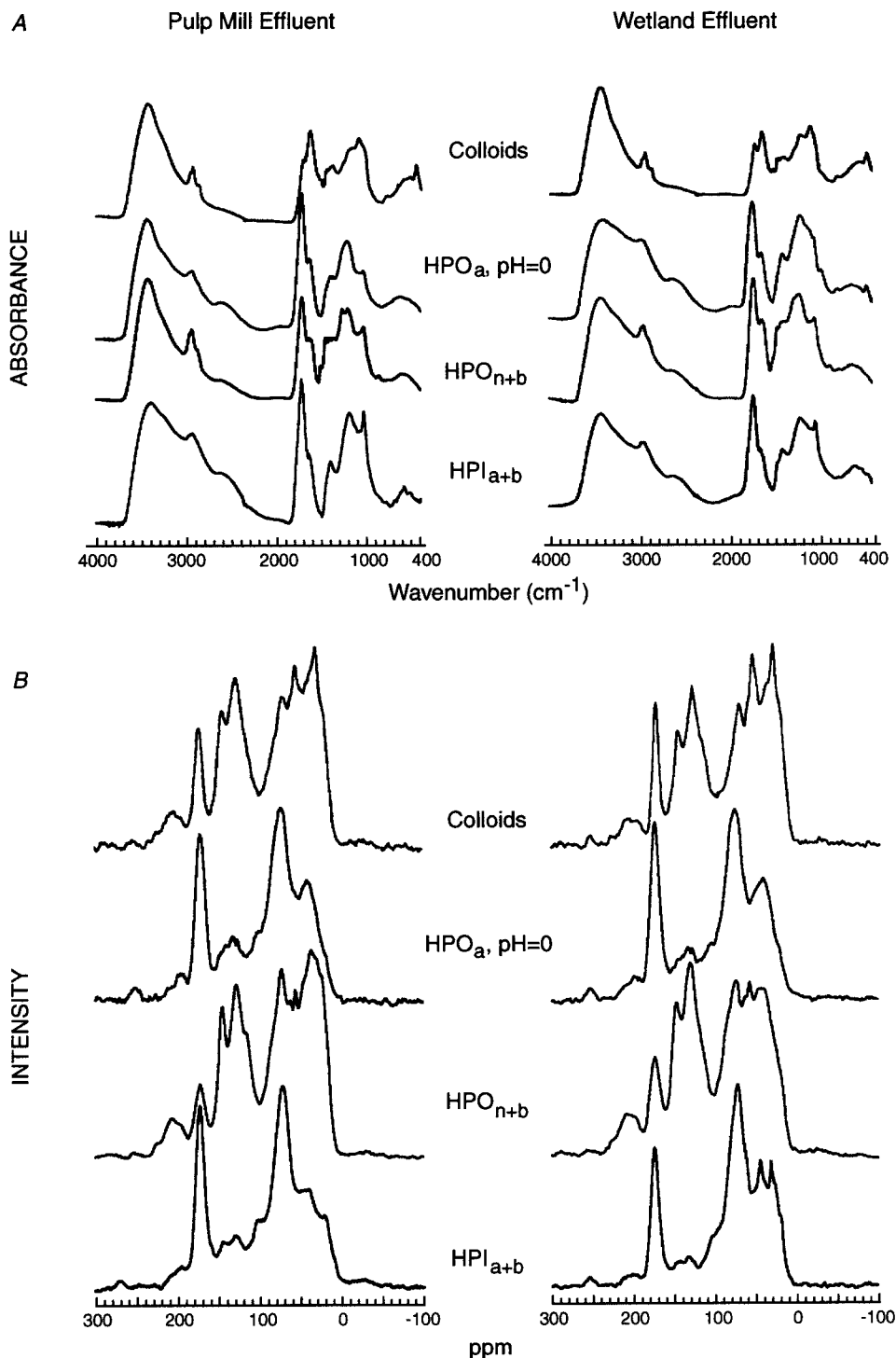
FIGURE 3. FTIR (A) and ^{13}C NMR (B) spectra for select DOM_p fractions from the Halsey, OR, Treatment Wetlands (Table 1) collected during April 1995.

content (70% of the TOC), although DOC concentrations also were significantly elevated. DOC decreased by 99% in the wetland effluent, slightly greater than dilution. Even though attenuated, the wetland effluent still had a DOC of 41 mg/L. SA_{254} increased from the initial low value in the dairy effluent. DOC_{mw} analysis indicated that 82–100% of the DOC was <30 000 Da and 30–57% was <3000 Da. LAS in the dairy effluent was >90 μg/L due to use of detergents in the wash down and concentrations decreased 98% in the wetland effluent, similar to DOC attenuation.

DOC_f analysis indicated that the dairy effluent was enriched in the HPO_a and HPI_n fractions with a significant amount of HPI_b. The DOM_p method was modified to isolate an extractable acid (EA) fraction. The dairy effluent was centrifuged, the supernatant was solvent extracted at pH 1 with methylene chloride, the methylene chloride was equilibrated with distilled water at pH 7 to extract organic acids as the sodium salts, and the aqueous phase was freeze-dried. The dairy effluent also had a significant colloid content that was effectively removed by wetland treatment. Elemental analysis (Table 5) indicated that the wetland effluent colloid fraction was enriched in nitrogen and that the HPO_a fraction was enriched in carbon and depleted in oxygen relative to the Arcata enhancement marsh effluent.

TABLE 7. Data for the Corvallis, OR, Wetland Site, April 1995[a]

site	SC (μS/cm)	DO (mg/L)	TOC (mg/L)	DOC (mg/L)	UV$_{254}$ (cm)	SA$_{254}$ (L mg^{-1} m^{-1})	DOC$_{mw}$ <100 000 Da (%)	<30 000 Da (%)	<10 000 Da (%)	<3000 Da (%)	<1000 Da (%)	LAS (μg/L)	EDTA (μg/L)	caffeine (μg/L)
dairy effluent	9820	<0.1	9,500	2,850	18.6	7	80	82	51	57	26	92.6	—	<0.1
wetland effluent	458	24.7	43.5	41.0	0.75	18	100	100	48	30	22	1.9	—	<0.1

	dairy effluent	wetland effluent
DOC$_f$ Analysis		
HPO$_a$ (%)	44	—
HPO$_b$ (%)	1	—
HPO$_n$ (%)	<1	—
HPI$_a$ (%)	0	—
HPI$_b$ (%)	12	—
HPI$_n$ (%)	44	—
DOM$_p$ Analysis		
total DOM (mg)[b]	982	597
DOC (mg/L)[c]	490	18
HPO$_a$ (%)	28	45
HPO$_n$ (%)	13	11
HPI$_a$ (%)	17	21
UHPI$_a$ (%)	6	13
HPI$_n$ (%)	5	10
EA (%)	32	—
colloid (%)[d]	446	—

[a] See Table 3 for explanation of abbreviations; EA, solvent extractable acids. [b] Total mass of fractions isolated from approximately 20-L sample. [c] DOC determined by multiplying mg/L DOM × 0.5. [d] Colloid fraction is not "dissolved" and thus not included when summing DOM fractions. Colloid (%) is calculated relative to total DOM.

FTIR analysis (Figure 4A) indicates that the colloid fraction in the dairy effluent was enriched in hydrocarbon and amide-1 carbon, indicating a lipid-rich glycoprotein material. The HPO$_a$ and HPO$_{n+b}$ fractions were similar and had a greater carboxylate and lesser hydrocarbon content than the colloid fraction and also contained an aromatic sulfonate peak. The HPI$_{a+b}$ fraction was enriched in amide-1. The dairy effluent EA fraction (data not shown) was a significant part of the total DOM and consisted primarily of benzoic acid, a preservative added to silage. The FTIR results for the wetland effluent colloid fraction indicated a decrease in hydrocarbons and an increase in CO content relative to the dairy effluent. The HPO$_a$, HPO$_{n+b}$, and HPI$_{a+b}$ fractions in the wetland effluent were similar to the dairy effluent, consistent with dilution being the primary attenuation process.

^{13}C NMR analysis (Figure 4B) of the dairy effluent colloid fraction indicates enrichment in aliphatic-1 carbon, and the wetland effluent colloid fraction was enriched in CEA, aliphatic-2, and aliphatic-3 carbon. The dairy effluent HPO$_a$ and HPO$_{n+b}$ fractions were highly enriched in aromatic carbon (reflecting a significant lignin and tannin component in the cow waste), and wetland treatment significantly attenuated the aromatic carbon while increasing CEA carbon. The dairy effluent HPI$_{a+b}$ fraction was enriched in CEA and aliphatic-3 carbon, and there was a decrease in aliphatic-1 carbon in the wetland effluent.

Discussion

The wetlands investigated in this study represent a wide range of source water strengths from secondary treated municipal wastewater (~10 mg/L DOC) to dairy parlor liquor (~3000 mg/L DOC). This range of concentrations presents an analytical challenge when trying to characterize the DOM, and the DOM$_p$ methods were custom designed to best accommodate the unique nature of each site. Although the amount and characteristics of the DOM varied among the wetlands, reflecting differences in the source waters, there were many similarities to natural DOM (31, 32). WWTP effluents are enriched in nitrogen-containing compounds relative to natural DOM and contain synthetic organic chemicals such as LAS and EDTA. Differences in DOM composition between sites were more prominent than differences within a site, although at each site transformations occurring during wetland treatment resulted in subtle changes in the DOM composition. Effluents from mature densely vegetated treatment wetlands had increased levels of humic substances derived from decaying vegetation in the wetlands relative to WWTP effluents, higher SA$_{254}$ values, and enrichment in oxygen and aromatic content. Systems with significant open water zones that support algae growth also had increases in DOM, but the molecular characteristics were different than that derived from vascular plants (more aliphatic), indicating the different autochthonous sources. This is further supported by data from Klamath Lake, Oregon, an algae dominated system (17). In agreement with Pinney et al. (4), there were seasonal trends in DOM transformations (both removal and inputs). During the summer, when biological activity is the greatest, both internal loading and biodegradation rates increase. When internal loading is greater than removal, DOM concentrations increase in the wetland effluent (25).

The major processes governing transformation of DOM in treatment wetlands include biodegradation, bio-uptake, sorption, volatilization, and photolysis. Although much is known about the environmental fate of specific organic contaminants (33) and natural organic matter (3, 34), less is known about the fate of DOM in treatment wetlands (4, 5). Sorption is a potential sink for hydrophobic organic chemicals and plays a role in the bioavailability of organic contaminants. WWTP effluents contain organic compounds with properties that allow volatilization and photolysis to be effective wetland removal mechanisms.

DOM in the Arcata primary clarifier effluent had distinct compositional differences and much higher concentrations than the secondary treated San Jacinto WWTP effluent; however, after facultative lagoon and treatment marsh polishing the composition was similar. This indicates that wetland treatment can produce an effluent similar to conventional secondary treatment. Removal of specific wastewater-derived contaminants such as LAS, EDTA, and
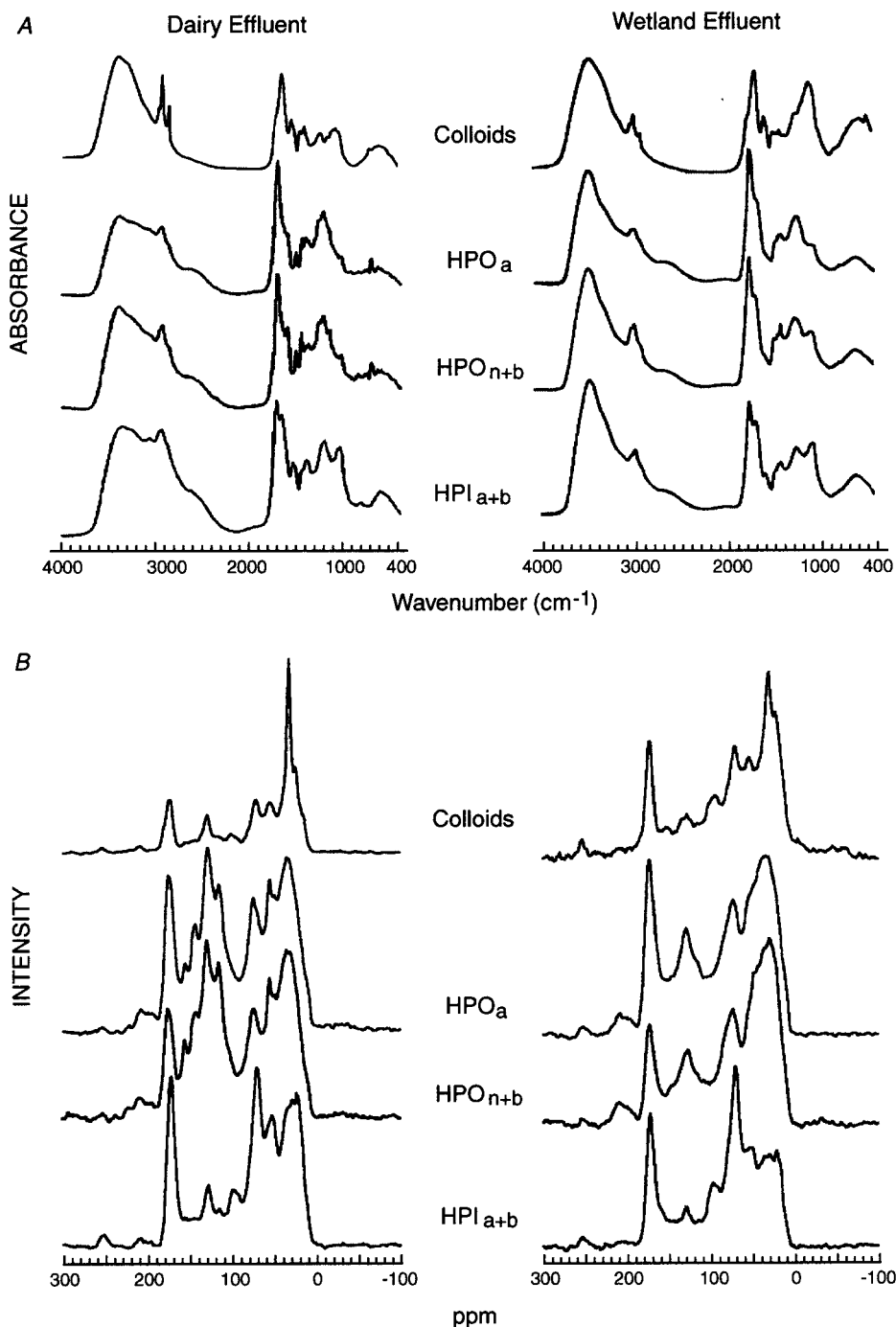
FIGURE 4. FTIR (A) and ^{13}C NMR (B) spectra for select DOM$_p$ fractions from the Corvallis, OR, Treatment Wetlands (Table 1) collected during August 1995.

caffeine appears to be a function of the geochemical environment in the wetlands. For example, there is little attenuation of LAS in wetland systems with low oxygen concentrations (San Jacinto) whereas LAS removal is nearly complete in oxygenated systems (Arcata), consistent with biodegradation being the primary LAS removal mechanism (6). On the other hand, EDTA is not readily biodegradable, and its primary removal mechanism is photolytic degradation (35), which is supported by the observation of greater attenuation in systems with more open water zones. Caffeine appears to have similar attenuation as LAS, but little is known about the actual removal mechanisms. In contrast to DOM concentrations in wetland effluents, which are a function of both production and removal rates and typically increase with increasing HRT, specific compound removal increases

with increasing HRT. Of course HRT also plays a role in other factors related to specific compound and DOM removal other than time for reactions to occur. For example, at longer HRT, geochemical conditions can change from aerobic to anaerobic, which in turn influences the rate of biodegradation for compounds such as LAS.

The Halsey pulp mill effluent had high concentrations of DOM consisting primarily of chlorinated and sulfonated lignin compounds and was compositionally distinct from WWTP effluent. In spite of the recalcitrant nature of the DOM, there was significant attenuation of DOC concentrations in the free water surface wetland effluents. The primary attenuation mechanisms appear to be sorption or precipitation as suggested by the selective removal of the HPO$_n$ fraction. Greater DOC removal by the open water and

vegetated cells relative to the rock bed indicates that additional processes are active in decreasing DOC concentrations. Photolysis has a greater effect in the open water and vegetated marshes than in the subsurface flow rock bed cell and may account, in part, for the greater DOC removal. Concentrations decreased more in the vegetated cell than in open water, indicating that plants enhance removal of DOC by biodegradation or uptake. Although individual constituents of the complex pulp mill effluent (*36*) were not determined, the FTIR, ^{13}C NMR, and elemental characteristics of DOM from the Halsey site are similar to those reported by Santos and Duarte (*37*). Even after wetland treatment, the effluent contained high levels of DOM.

The Corvallis dairy effluent was significantly different than WWTP and pulp mill effluents; the DOC was almost 3000 mg/L and consisted of organic matter originating as fresh cow waste. Operating conditions of the wetland significantly decreased DOM concentrations, in agreement with Tanner et al. (*38*), who investigated constructed wetlands for treating dairy wastewater and concluded that treatment wetlands effectively remove BOD, TSS, and nutrients. Although dilution appeared to account for most of the decrease in concentration, changes in the molecular characteristics of the DOM in the wetland effluent indicated that transformations were occurring.

This investigation shows that the DOM content of wastewater used to supply treatment wetlands and receiving streams is complex and varies with the nature of the source. Biotic and abiotic processes occurring in treatment wetlands act to transform DOM by selectively removing certain constituents and adding new components. The hierarchical analytical approach used in this investigation proved useful in directly measuring the DOM transformations. These transformations have notable implications for the subsequent reuse of the water, such as increased chlorine reactivity of DOM produced in treatment wetlands relative to WWTP effluents (*4, 39*).

Acknowledgments

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