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Environmental Chemistry

DISSOLVED OXYGEN CONCENTRATIONS IN FLORIDA'S HUMIC-COLORED WATERS AND WATER QUALITY STANDARD IMPLICATIONS

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Abstract: *The Florida Department of Environmental Regulation has established detailed dissolved oxygen standards for the various classes of surface water in the state. The results of this study and a review of the literature reveal that many natural humic-colored aquatic systems (usually Class III waters) rarely meet the established 5 mg/L criteria. We believe, based on our studies, that these conditions are natural and do not result from organic pollution. In view of this, we believe a review of the current DER Standard, for humic-colored waters only, is in order.*

Dissolved oxygen is probably the most important and frequently used indicator of water quality, since it is easily understood and relatively simple to measure. Dissolved oxygen is essential to the metabolism of organisms for aerobic respiration and when it is depleted the system becomes anaerobic, organic matter accumulates and most organisms die. When this happens, the apparent effects to the public are fish kills and loss of recreational amenities.

In an attempt to avert problems such as these, the State of Florida has established standards for the dissolved oxygen content for surface waters, based on the primary use of that water (Florida Department of Environmental Regulation, 1970). In summary, these standards state that Class I Waters (potable water supplies) and Class III Waters (recreation) should maintain dissolved oxygen levels above 5 mg/L, while Class II Waters (shellfish propagation and harvesting) and Class IV Waters (agricultural supplies) should maintain average 24-hour concentrations of not less than 5 mg/L and 4 mg/L, respectively. Also, the concentrations for Class II and Class IV Waters should never be less than 4 mg/L and 3 mg/L, respectively. Class V Waters (navigation, utility and industrial use) shall not have concentrations below 2 mg/L.

It can be seen from the above regulations that the standard is very detailed, sometimes requiring 24-hour diurnal measurements. Unfortunately, many aquatic systems in Florida do not meet these standards. Lakes, swamps, and streams that are highly colored with humic compounds often never reach oxygen saturation. In view of this fact, the purpose of this paper is to show that low dissolved oxygen conditions are typical of many humic-colored aquatic systems in Florida and to suggest that the dissolved oxygen standard should be revised.

Site Descriptions — Four sites in east and central Florida having differing degrees of humic color were investigated (Fig. 1).

Three sites were located in south Florida and are under the jurisdiction of the South Florida Water Management District (SFWMD). They are Armstrong Slough in Osceola County, Belcher Canal (C-25) in St. Lucie County and Chandler Slough in Okeechobee County. Armstrong Slough is located about six miles south of State Road 60 east of the Kissimmee River and drains approximately 22,000 acres of mixed use agricultural land, pasture and native vegetation. Major land uses are light to moderate density cattle grazing and citrus. The tributary channels drain a marsh area, which was expanded in 1980 by the SFWMD, and is now some 453 acres in size (Goldstein, 1981). The sampling locations were located at a gaging station 50 meters downstream of the marsh in the major drainage channel.

Chandler Slough is the largest tributary of the Kissimmee River (Federico et al., 1978) and is a natural flood plain marsh which is somewhat channeled near U.S. 98, approximately four miles east of the Kissimmee River. Land in the basin is primarily occupied by cattle ranches and open wetlands. Approximately 80 percent of the land is unimproved, improved and ditched pasture and 20 percent is marsh and swamp. The sampling location was at the north bridge of U.S. 98 which crosses the partially channeled area of the slough.

Belcher Canal, in St. Lucie County, is relatively deep with steep banks and drains approximately 83,500 acres, with 52 percent being improved pasture, 23 percent citrus and the rest mainly forest uplands and wetlands. The canal generally flows east through a spillway into the Indian River near Ft. Pierce. The location for sampling was from the Taylor River bridge crossing the canal approximately two miles west of the spillway.

The fourth study site was located in central Florida in the Upper St. Johns River Basin near the entrance to Lake Washington. Drainage in this area is by sheet flow through marsh and wetlands and through drainage canals used for improving pasture and agricultural lands. The river was sampled near the U.S. 192 bridge, at the Camp Holly Fish Camp. This site was chosen as a sampling location because of the large number of previous dissolved oxygen studies com-

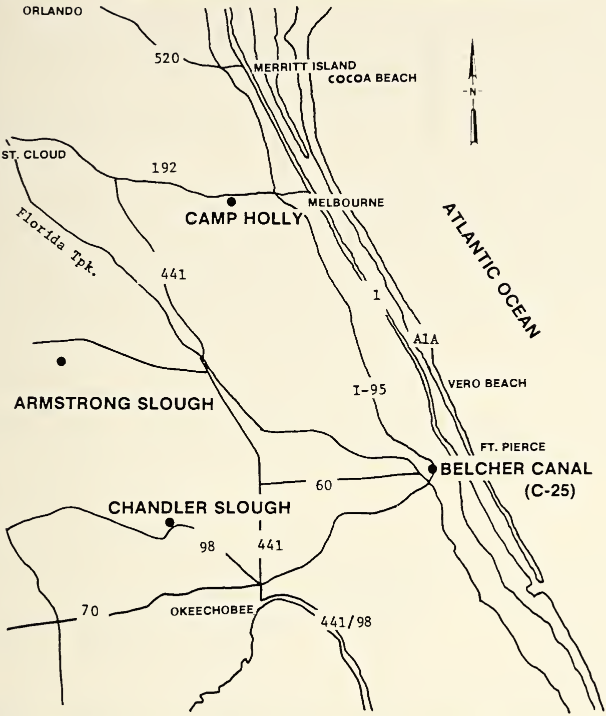

Fig. 1. Site locations, major highways and cities in the east central Florida study area.

pleted there. At this location the river has formed a proper channel and flows north into Lake Washington, the major source of drinking water for south Brevard County.

The selection of sites described above represents, in part, the variation in fresh water systems found in central and southeast Florida. They are Chandler Slough as a natural marsh, Belcher Canal as a man-made drainage system, Armstrong Slough as part natural and part man-made marsh, and Camp Holly as a natural riverine-marsh system.

METHODS — Chandler Slough, Belcher Canal, and Armstrong Slough are Class III waters; the St. Johns River at Camp Holly is Class I. Each of the sites were sampled three times during 1983, with the exception of Camp Holly, which was sampled four times. The first set of samples were taken during the winter period, the second during early summer, and the last during late summer in order to obtain a seasonal variation.

All of the source and sink terms in the oxygen balance were measured according to procedures outlined by Roberts (1983), but only the most relevant data are presented as it is not the objective of this paper to present the budgets in detail. Community metabolism, as presented in this report, was measured by the free-water diurnal oxygen method described by Odum and Hoskin (1958). This method measures the diurnal changes in the concentration of oxygen in an aquatic system, relates these changes to saturation based on temperature, and corrects for atmospheric diffusion. Dissolved oxygen concentration and temperature were determined at various depths every two to three hours over a 24-hour period. In order to eliminate the problems of graphical estimation and the assumption of constant night respiration inherent in the Odum technique, a United States

Geological Survey computer program (Stephens and Jennings, 1976) was used to calculate net daytime productivity, night respiration and total community metabolism. Normally, the user inputs a diffusion constant to correct the community productivity values. An equation for the reaeration coefficient (K_2) based on the Velz rational method (Velz, 1970) was derived by McCutcheon and Jennings (1982) and used in this study.

It should be noted that the Odum methodology allows for both single station and upstream/downstream station techniques. In this study, it was assumed that each site either had similar characteristics upstream or there was insufficient flow to affect the site. Because of this, the single station technique was used.

In order to insure that readings of dissolved oxygen taken by the Leeds and Northrup portable dissolved oxygen meter were accurate, comparisons between oxygen concentrations determined by the Modified Winkler, Full Bottle Titration Technique (EPA, 1976) and readings obtained by the meter were frequently made during the study. The values obtained from both methods were always within 0.2 mg/L. Dissolved organic color was measured by absorption of filtered sample water on a Perkin-Elmer double beam spectrophotometer-Coleman Model 124. Incoming solar radiation (insolation) was continuously recorded during field sampling at each site with a Weather Measure Model R401 mechanical pyranograph. An accurate and relatively easy method for determining total and ferrous iron concentrations has been perfected (ASTM, 1977). The procedure uses an ammonium acetate solution to buffer the reactants to pH 3.5-4.0; hydroxylamine hydrochloride reduces ferric iron to ferrous iron for total iron determination with bathophenanthroline as a colored complexing ligand for ferrous ions. The sample is preserved with concentrated HCl (2 ml/100 ml sample) and stored in dark plastic bottles at 4°C and then filtered through a 0.45 μm membrane in the lab prior to analysis. Therefore, the values obtained by this procedure may be considered as "filtrable, acid-hydrolyzed" ferrous and total iron.

TABLE 1. Average dissolved oxygen and related parameters at the study sites.[1]

Site	Average Dissolved Oxygen (mg/L)	Temperature (C°)	Saturation (%)	Color (CPU)
Armstrong Slough				
3/3/83	4.8	21.0	55.3	335
6/29/83	1.6	29.1	21.0	380
8/17/83	2.2	27.1	27.5	290
Belcher Canal				
2/3/83	6.0	17.9	63.6	105
6/12/83	2.9	28.7	38.2	170
8/5/83	1.8	29.2	23.9	220
Chandler Slough				
2/24/83	3.9	19.4	42.7	420
6/20/83	1.6	27.3	20.6	190
8/14/83	1.2	25.1	15.3	445
Camp Holly				
2/17/83	4.9	15.4	49.2	245
3/21/83	3.8	21.0	43.5	305
5/26/83	5.0	28.9	66.2	300
8/1/83	4.4	29.1	58.5	335
Average (all sites)	3.4	24.6	40.4	280
ST. DEV. (all sites)	± 1.6	± 4.9	± 17.5	± 99.5

[1]Averages for each date are from one meter depth increments over a 24-hr period.

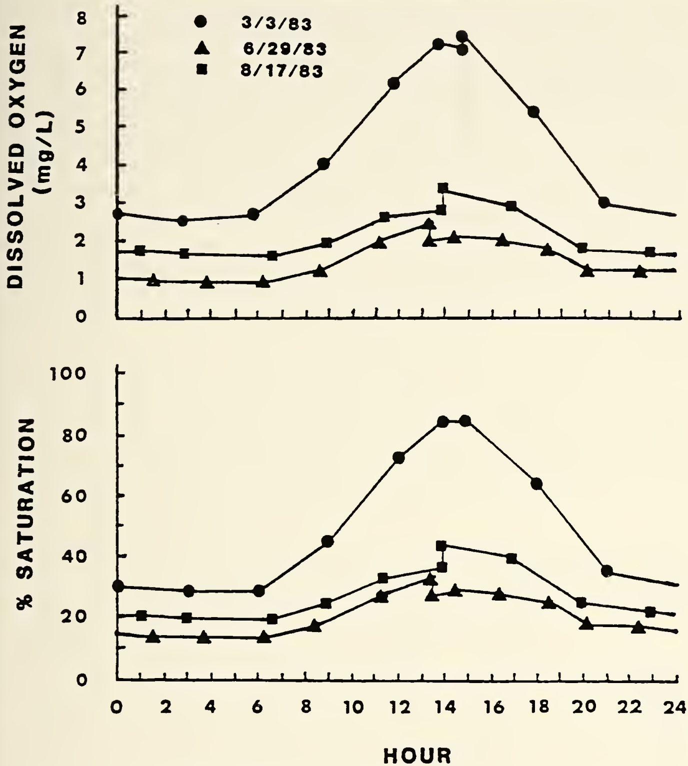

FIG. 2. Armstrong Slough diurnal oxygen curves.

RESULTS AND DISCUSSION — As can be seen in Table 1, the 24-hour average oxygen levels at sites in this study varied from a summer low of 1.2 mg/L in Chandler Slough, a natural drainage marsh, to 6.0 mg/L in Belcher Canal, a man-made drainage structure. The extremely flat nature of the diurnal curves, except for Armstrong Slough (3/3/83), is shown in Figs. 2 through 5. These figures show that the systems are generally very undersaturated with respect to oxygen.

Oxygen budgets were completed on each system by Roberts (1983) and the parameters investigated (primary production, respiration, sediment demand, chemical consumption and diffusion) point to the dominance of oxygen depleting processes over oxygen producing processes. Sediment uptake was found to be a significant oxygen sink in these systems, while diffusion was an important source. Pollutional sources at these sites are not high, as revealed by the variable but generally low BOD levels shown in Table 2, and indicate that the low oxygen levels must be considered as normal ambient levels reflecting the natural oxygen budgets operating in these systems. The low light penetration through the colored waters severely limits production from plankton and submerged macrophytes, and the most significant supply of oxygen was from diffusion from the atmosphere as a result of the undersaturated conditions of the waters. Apparently, it is diffusion that nearly balances the metabolism of these systems and allows them to function aerobically. The low to negative 24-hour community metabolism values calculated for these areas are shown in Table 3. These values reflect the complete biological and physical sources and sinks of oxygen in the system, including diffusion, and give an estimate of net gains or losses of oxygen in the system.

Other investigations in humic-colored waters of the state have shown undersaturated and low dissolved oxygen (<5.0 mg/L) conditions. Diurnal oxygen measurements have been made since 1980 on the Upper St. Johns River at Camp Holly, the same site used in this study (Belanger et al., 1983). The curves, presented in Fig. 6, show very little oxygen fluctuation, and

TABLE 2. Measured carbonaceous and total biochemical oxygen demand levels and rate constants at the study sites.

	Carbonaceous BOD		Total BOD		Total
Site	L (mg/L)	k (1) (1/day)	L (mg/L)	k (1/day)	Uptake (gm/m^2-d)
Armstrong S					
3/3/83	3.8	0.15	3.6	0.15	0.91
6/29/83	8.2	0.05	11.5	0.04	0.71
8/17/83	4.3	0.08	4.7	0.13	0.74
Belcher C					
2/3/83	5.6	0.06	7.9	0.04	1.06
6/12/83	9.2	0.03	17.2	0.02	1.07
8/5/83	4.5	0.12	8.9	0.06	1.71
Chandler S					
2/24/83	4.7	0.04	4.3	0.05	0.67
6/20/83	11.2	0.15	19.1	0.10	6.00
8/14/83	5.8	0.08	6.3	0.07	1.44
Camp Holly					
2/17/83	2.5	0.20	2.4	0.17	0.99
3/21/83	8.5	0.05	9.2	0.05	0.87
5/26/83	5.6	0.14	5.8	0.20	2.22
8/1/83	3.2	0.11	4.6	0.11	1.04
Average (all sites)	5.9	0.10	8.1	0.09	1.49
ST. DEV.	± 2.6	± 0.05	± 5.1	± 0.06	± 1.41

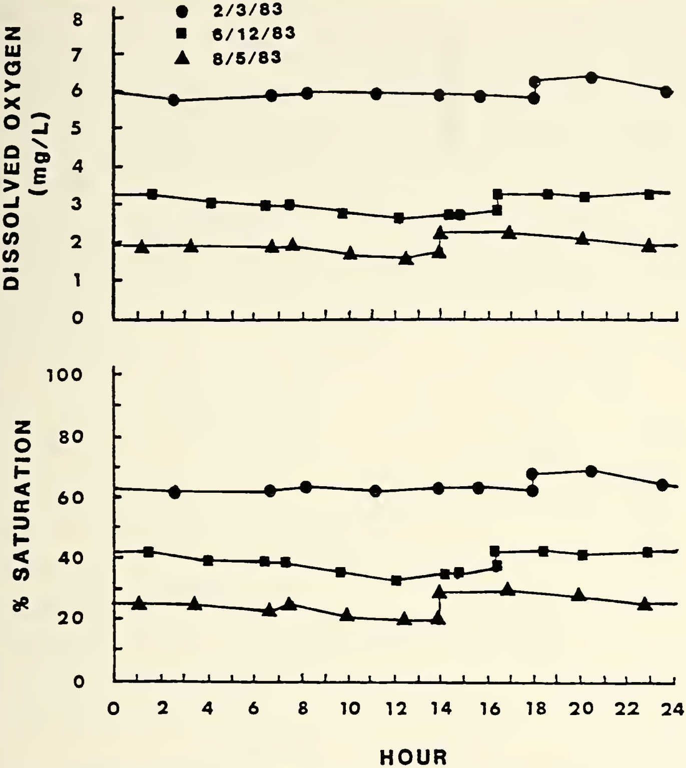

FIG. 3. Belcher Canal diurnal oxygen curves.

undersaturated conditions occur most of the time. Table 4 presents the chemical data associated with the diurnal curves. Generally, a low color corresponds to a high dissolved oxygen saturation, while high color is related to low oxygen saturation values ($r = .82$; $p < .01$). Also, total iron increases with color as stable iron-humic complexes are formed ($r = .91$; $p < .01$).

In their study of oxygen consumption by a photochemical Fe(II)-Fe(III) catalytic cycle in humic colored waters, Miles and Brezonik (1981) also found low oxygen levels coupled with high color and iron levels. Data from five of their sites are shown in Table 5. The cycle consists of the photoreduction of Fe(III) to Fe(II) by humic matter and subsequent oxidation of Fe(II) back to Fe(III) by dissolved oxygen. Since humic material forms very stable complexes with iron, which results in a strong correlation of soluble iron

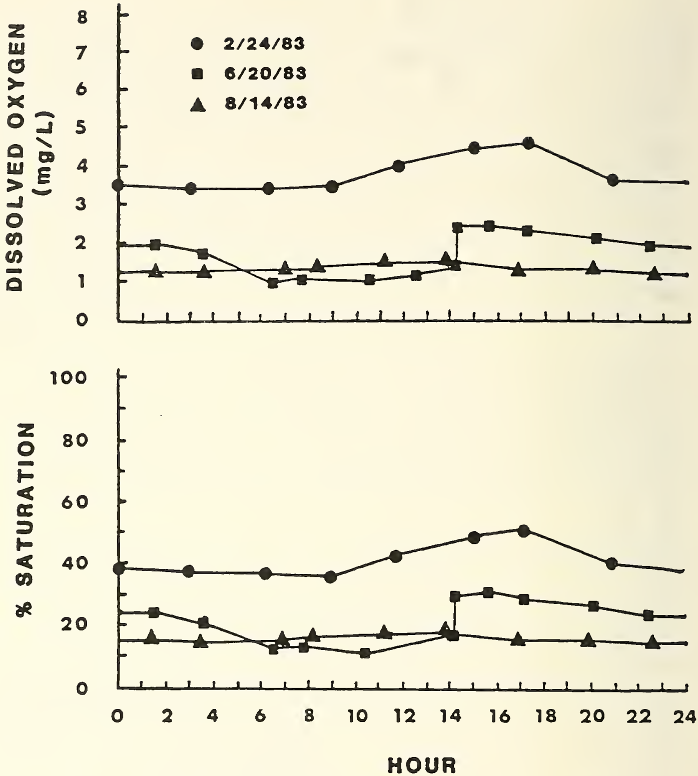

FIG. 4. Chandler Slough diurnal oxygen curves.

concentration and humic color, it is possible that this chemical oxygen consumption mechanism may be more important than biological respiration in highly colored swamps and canal waters. This uptake mechanism should be investigated further. Experiments by Roberts (1983), in which the uptake rates of poisoned and unpoisoned light and dark bottles were recorded, did not prove this mechanism was occurring at our sites and results were very erratic. We feel, however, that the occurrence of this catalytic cycle should be further investigated to prove conclusively its occurrence or absence.

Dierberg and Brezonik (1984) have done extensive chemical studies on the humic-colored natural swamp waters of a cypress dome in the Austin Cary Memorial Forest in Alachua County. They reported dissolved oxygen values consistently lower than saturation levels and never exceeding 6.8

mg/L with a mean of 2.0 mg/L. Soluble iron levels were found to be high with a range of 150 to 600 μg/L and a mean of 370 μg/L.

In a survey of the water quality of the Kissimmee-Okeechobee watershed, Federico and Brezonik (1975) found highly colored water with low dissolved oxygen concentrations in all areas of their study. Table 6 shows the chemical characteristics of several of the studied sloughs that drain into the lower basin of the Kissimmee River. High color was attributed mainly to leaching of humic and tannic substances within the marshes. These substances can chelate metals, lower pH, and decrease light transmittance. The low dissolved oxygen levels may be due to BOD of cattle droppings, but the values are typical of those found in natural marsh areas. Seasonal effects were generally found to be such that higher flows in the summer produced higher color readings and lower dissolved oxygen, which was attributed to increased runoff.

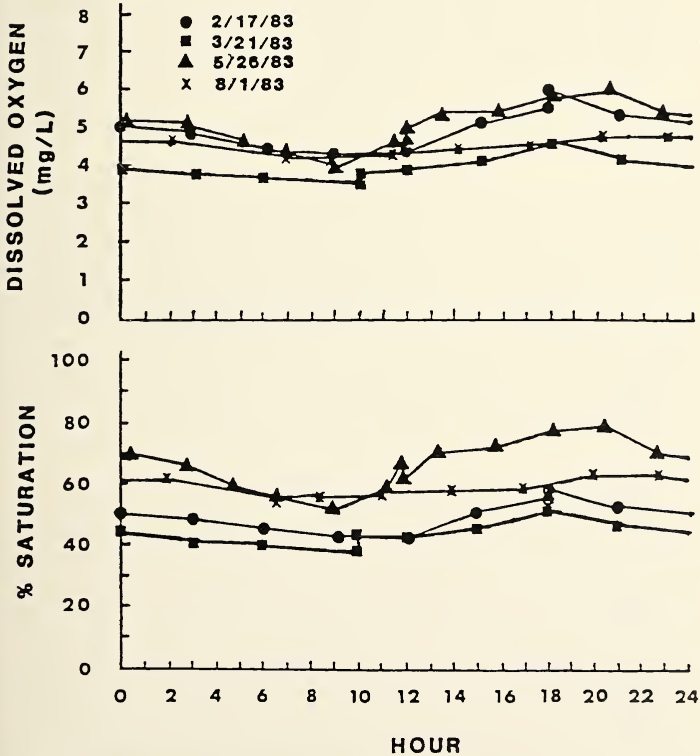

Fig. 5. Camp Holly diurnal oxygen curves.

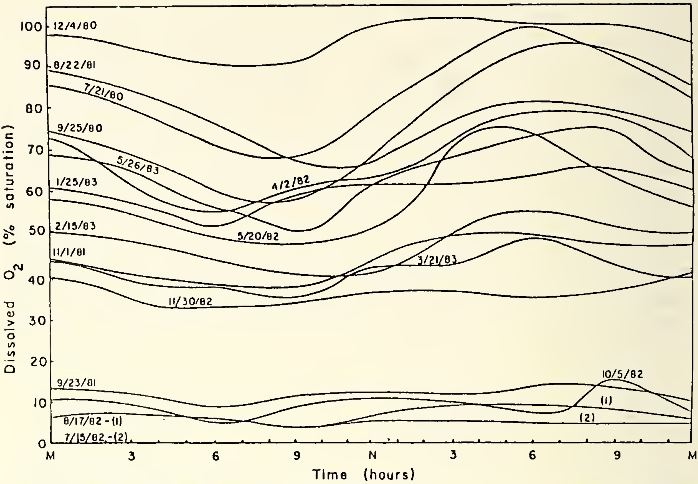

FIG. 6. Diurnal oxygen curves (% saturation) at Camp Holly in the upper St. Johns River (from Belanger *et al.*, 1983).

TABLE 3. Total System 24-hr community metabolism values for the study sites.

Site	Community metabolism (gm O_2/m^2-day) (plus diffusion)
Armstrong Slough	
3/3/83	−0.4
6/29/83	0.7
8/17/83	−0.6
Belcher Canal	
2/3/83	−1.5
6/12/83	−1.2
8/5/83	−1.8
Chandler Slough	
2/24/83	0.1
6/20/83	−3.0
8/14/83	0.3
Camp Holly-St. Johns River	
2/17/83	−0.8
3/21/83	−0.6
5/26/83	0.6
8/1/83	0.2

TABLE 4. Water chemistry and solar radiation data for diurnal curves presented in Figure 6.

Date	Color (CPU)	Total Fe (mg/L)	FeII (mg/L)	Solar Radiation (Kcal/m²/hr)
12/4/80	60	0.10	--	--
7/21/80	35	0.03	--	--
9/25/80	38	0.04	--	--
8/22/81	65	0.08	--	32.5
9/23/81	232	0.18	--	--
11/1/81	265	0.20	--	--
4/2/82	270	0.21	0.09	
5/20/82	394	0.24	0.15	
7/15/82	440	0.27	0.25	22.8
8/17/82	438	0.42	0.32	19.8
10/5/82	401	0.37	0.28	23.4
11/30/82	332	0.27	0.18	13.8
1/25/83	243	0.21	0.14	15.6
2/15/83	243	0.26	0.08	1.4
3/21/83	304	0.30	0.13	25.3
5/24/83	269	0.17	0.14	31.5
Average	252	0.21	0.18	20.7
STD. DEV.	± 134	± 0.11	± 0.08	± 9.6

A final example familiar to the authors is that of Goat Creek, an undeveloped naturally colored drainage creek discharging into the Indian River, south of Palm Bay, Florida. This creek was chosen for background data by the DER in 1981 for comparison with Turkey Creek water quality data during a review of NPDES permit applications submitted by the Harris Corporation, a discharger to Turkey Creek. The dissolved oxygen levels recorded in Goat Creek, however, were similar or lower than Turkey Creek, a much less colored creek located several miles to the north in a highly developed and urbanized watershed. Diurnal dissolved data indicated that the colored Goat Creek did not meet the 5 mg/L standard at most sites (Post, Buckley, Schuh and Jernigan, 1981).

CONCLUSIONS — In view of data acquired in this study, and a brief review of the literature, it seems the 5.0 mg/L dissolved oxygen standard for these and similar aquatic systems is unrealistic. A better approach would be to set standards based on the continued determination of the uniqueness of each system, as this study has begun. Then, individually, the application of the water quality standard for dissolved oxygen could be assessed and modified on a case-by-case basis. This approach would be expensive and time consuming, however, and our study indicates that if a uniform water quality standard for humic colored water is to be established and maintained, it should be lower than the present 5 mg/L standard existing for Class III water.

ACKNOWLEDGMENTS — Data used in this paper were largely obtained from a project funded by the South Florida Water Management District. The assistance of the District staff was greatly appreciated.

TABLE 5. Oxygen and chemical measurements on some colored waters in Florida (after Miles and Brezonik, 1981).

Water Body	(County)	DO(mg/L)	Color (CPU)	Total Fe (μg/L)
L. Mise	Alachua	3.8	350	1500
Calf Pond	Alachua	1.1	300	300
Burnt Pond	Alachua	5.8	105	100
L. Monroe	Seminole	3.8	380	300
L. Jessup	Seminole	3.5	270	100

TABLE 6. Dissolved oxygen and chemical data in Kissimmee-Okeechobee Watershed (after Federico and Brezonik, 1975).

	Dissolved Oxygen (mg/L)			Color (CPU)			pH		
Slough	Average	Low	High	Average	Low	High	Average	Low	High
Ice Cream	5.8	3.9	9.3	102	32	280	7.0	5.2	8.1
Blanket Bay	3.8	0.5	9.2	178	75	320	6.9	6.5	7.3
Packingham	4.8	0.2	14.2	174	78	330	6.5	5.9	6.8
Buttermilk	3.2	0.3	8.3	158	55	365	6.4	5.7	7.5
Skeeter	4.8	0.1	8.1	86	50	205	7.1	6.7	7.4
Armstrong	5.3	2.9	7.6	90	50	240	6.4	6.6	7.5
Chandler Upper Reach	2.1	--	--	148	--	--	7.3	--	--
Chandler Lower Reach	3.5	--	--	123	--	--	7.3	--	--

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