

Relationship of Chlorophyll *a* Concentration to Seasonal Water Quality in Lake Manatee, Florida¹

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One adverse effect of nutrient enrichment in surface water bodies is the occurrence of nuisance “algal” blooms. Of primary concern in Lake Manatee, Florida are the cyanobacteria - *Anabaena circinalis* and *Oscillatoria* sp. Such blooms cause problems for drinking-water reservoirs, since they produce an earthy, musty odor and can make the taste of the water unpleasant (Barnhart 1980; Raman 1985; Hawkins and Griffiths 1987). Taste and odor problems have been quantified by the presence of two organoleptic compounds, 2-methylisoborneol (2-MIB) at concentrations greater than 12 ng L⁻¹ and geosmin at concentrations greater than 7 ng L⁻¹ (Simpson and MacLeod 1991). These compounds are actually metabolites produced by *Anabaena* and *Oscillatoria*, and some actinomycetes (Izaguirre et al. 1983). Chlorophyll *a* (Chl *a*) is often used as an estimate of algal biomass, with blooms being estimated to occur when Chl *a* concentrations exceed 40 µg L⁻¹. Investigators have shown that there is often a strong correlation between total phosphorus (TP) and algal biomass (Sakamoto 1966; Dillion and Rigler 1974; Jones and Bachmann 1976; Carlson 1977). This suggests that P may be the element controlling algal growth. However, lakes surrounded

by rich phosphate deposits and P-containing soils may be N-limited. Existing equations using P and Chl *a* as independent variables may inadequately estimate algal biomass under such circumstances. Canfield (1983) developed a Chl *a* equation using samples from 223 Florida lakes, 27% of which were considered N-limited. Because of the long growing season in Florida, these samples were taken year-round (August 1979 through September 1980). Chl *a* evidenced significant correlations with both TP ($r = 0.79, p < 0.01$) and total N (TN) ($r = 0.87, p < 0.01$). The TN association was evident when plotting Chl *a* concentrations versus TP. Total P concentrations above 100 µg L⁻¹, which for most lakes yielded TN/TP ratios less than 10, produced a slope change of the TP / Chl *a* linear relationship. This suggests that P is the limiting nutrient below TP levels of 100 µg L⁻¹, and that N is the limiting nutrient above that concentration.

The ability to identify significant parameters and predict subsequent algal blooms with the use of a Chl *a* equation could be an important lakewater management tool. Both chemical and physical controls can be used to prevent or remove algae or

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algae byproducts from the water. Copper sulfate is a common algicide used to control algal density (Raman 1985; Hawkins and Griffiths 1987), whereas activated carbon is used subsequently to remove undesirable tastes and odor. The cost to treat Lake Manatee Reservoir water with activated carbon where blooms have occurred can exceed \$14,000 per day (Manatee County Public Works Department, personal communication). Activated carbon also must be replaced frequently, because its absorption efficiency is decreased by high concentrations of humic substances found in waters such as the Lake Manatee Reservoir. Such factors make the reduction of algal density more of an economic than a potential health issue.

The primary objectives of this study were to determine if a significant relationship existed between levels of selected water quality parameters and Chl *a* concentration in Lake Manatee, and to develop a predictive equation for estimating when water quality conditions were conducive to high Chl *a* levels.

Site Description

The Lake Manatee watershed is located in the northeast sector of Manatee County, Florida. Lake Manatee Dam was constructed in 1967, and is located 24 miles upstream from the entry point of the Manatee River into Tampa Bay. The area of the watershed is 33,846 hectares, with its 729-hectare reservoir serving as the principal potable water source for over 265,000 people in Manatee and Sarasota Counties. The reservoir has a relatively shallow depth, averaging 3.9 meters, and is well-mixed with little or no stratification throughout the year (Rampenthal and Ferraro 1987). While many lakes in Florida are regarded to be P-limited, Lake Manatee is considered N-limited due to the influx of phosphate from phosphatic deposits in its upper reaches (Gee and Jensen 1984) where phosphate mining is a commercial enterprise. The reservoir is a drinking water source, and it must meet the stringent State of Florida surface water quality criteria for Class I waters; therefore, any deterioration of water quality becomes a public concern.

Materials and Methods

Monthly water samples were collected from Lake Manatee February 1990 to November 1992 at eight sampling stations located at strategic points in Lake Manatee. Water quality parameters measured over this time period included pH, electrical conductivity (EC), water temperature, dissolved oxygen, TP, reactive P, TN, chloride, fluoride, lead, copper, alkalinity, total Kjeldahl N (TKN), ammonia, nitrate-N, nitrite-N, sulfate, turbidity, Chl *a*, and pheophytin *a* (a degradation product of Chl *a*). Samples were collected in the mid-morning to early afternoon with a vertical-profile Niskin sampler. All water samples, except the sample for Chl *a*, were collected from the surface, middle, and bottom of the water column, mixed, placed in sample bottles, preserved according to Standard Methods (1989), and kept at 40°C until analyzed. The sample for Chl *a* was taken from a depth equal to 1.5 times the black Secchi disk transparency depth for water clarity. Analytical methods used to measure specific parameters were performed according Standard Methods (1989). General statistics of the surface water quality parameters, and Class I Surface Water Standards are given in Table 1.

Pearson's and Spearman's correlation coefficients were used for measuring the strength of a linear relationship between quantitative variables and to build a regression equation for Chl *a* concentrations. Pearson correlations are strongly sensitive to data that deviate from normality and are strongly influenced by observations that are extreme. Spearman's correlation, a nonparametric rank-based correlation, can resolve the problem of unduly influential observations. The day of sampling affected the relationship between parameters in some cases, and therefore, partial correlation coefficients were used. Log_{10} transformations of each variable were also analyzed using the same procedures.

Results and Discussion

Pearson's and Spearman's correlation coefficients for all parameters (Table 2) with a p -value < 0.2 were considered to have a significant initial relationship to Chl *a*, and were subsequently tested as independent variables in the equation. The

variables that did not contribute appreciably to the predictive ability of the equation were removed. There were 267 total observations in the data set that included Chl *a* for possible use in the equation.

A sensitivity test was performed to determine which parameters had the most influence on the equation. Most to least influential parameters were water temperature, electrical conductivity, TN/TP ratio, nitrate-N, and nitrite-N. The resultant prediction equation was:

$$\log \text{Chl } a = -3.04 - 0.25 \log \text{NO}_3 + 0.58 \log \text{NO}_2 + 0.45 \log \text{TN/TP} + 1.582 \log \text{Temp} + 0.65 \log \text{EC} [1]$$

where,

Chl *a* = concentration of chlorophyll *a* ($\mu\text{g L}^{-1}$)

NO_3 = concentration of nitrate-N (mg L^{-1})

NO_2 = concentration of nitrite-N (mg L^{-1})

TN/TP = ratio between concentration of total N (mg L^{-1}) and total P (mg L^{-1})

Temp = water temperature ($^{\circ}\text{C}$)

EC = electrical conductivity ($\mu\text{mhos cm}^{-1}$).

Despite the relatively low coefficient of determination ($r^2 = 0.41$), the relationship described by this equation was highly significant ($p = 0.0001$).

Data collected in 1993 were used to test the above equation as well as similar equations developed by Dillion and Rigler (1974), Jones and Bachmann (1976), and Canfield (1983). Equations using only TP as the independent variable were not significantly effective for predicting Chl *a* concentration for Lake Manatee (Table 3). Although the equations developed by Canfield (1983) using TN with or without TP did show a statistically significant relationship, the r^2 values were so low (0.07 and 0.11, respectively) that the equations were not considered adequate for Lake Manatees situation. Canfield's equation using only TN as an independent variable (Table 3, c) was unable to predict actual Chl *a* concentrations (Figure 1). In contrast, actual versus

predicted values for Chl *a* concentrations using the 1993 data set in conjunction with the equation developed in this study gave good prediction (Figure 2).

During the course of study, frequent additions of copper sulfate were a possible source of interference with data used for creating a Chl *a* equation for Lake Manatee. The algicide would likely reduce Chl *a* concentrations subsequent to such additions, thus giving misleading relationships with nutrient content. To test this effect, three additional prediction equations were created by removing a given Chl *a* measurement if copper sulfate treatment had occurred within either 2, 6, or 12 days prior to water sampling. These equations were similar to the original equations.

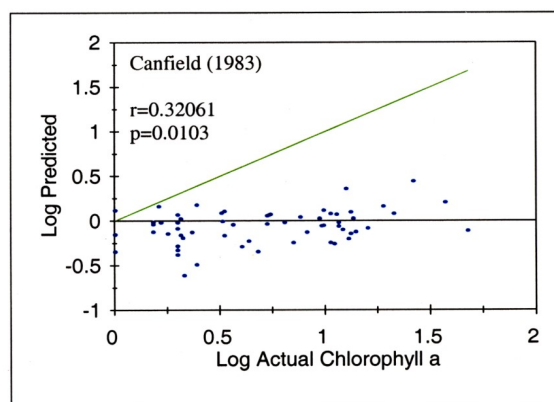


Figure 1.

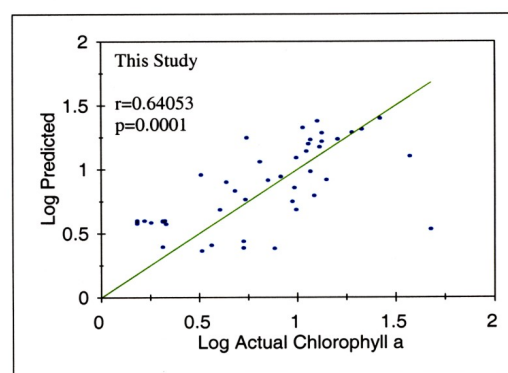


Figure 2. Plot of actual versus predicted Chl *a* concentrations using 1993 Lake Manatee water quality data and the equation developed in this study (Table 3).

Conclusions

None of the previously published Chl *a* prediction equations adequately described the

relationship between Chl *a* and nutrient levels in Lake Manatee. This was true even for an equation created specifically using data from Florida lakes (Canfield 1983). Our study helps to identify those water quality parameters which evidence a significant relationship to algal production in Lake Manatee, including inorganic N (nitrate and nitrite), water temperature, electrical conductivity, and TN/TP ratio. Other parameters had significant correlation with Chl *a* concentration as well, but did not significantly contribute to the prediction capability of the Chl *a* regression equation.

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Table 1. General Statistics of Surface Water Quality Parameters for Lake Manatee (1983-1992), and Class I Surface Water Standards (where available).

Parameter	Units	Min	Means	Max	StdDev	N	Class I Standard*	Percent Exceed
pH		5.00	6.96	.50	0.5	763	6.0-8.5	3%
Electrical Conductivity	$\mu\text{mhos cm}^{-1}$	42	199	822	98.5	737	1275	0%
Temperature	$^{\circ}\text{C}$	14.5	25.0	39.0	.5	792	-	-
Dissolved Oxygen	mg L^{-1}	0.30	6.1	12.8	2.0	61	5 (min)	29%
Total Phosphorus	mg L^{-1}	0.06	0.25	1.01	0.1	768	-	-
Chloride	mg L^{-1}	0.16	14.92	30.30	4.5	507	250	0%
Fluoride	mg L^{-1}	0.05	0.24	0.71	0.10	483	1.5	0%
Total Hardness	mg L^{-1}	23.1	41.9	67.5	11.1	52	-	0%
Lead	$\mu\text{g L}^{-1}$	1.0	4.4	46.0	5.4	445	30.0	<1%
Copper	$\mu\text{g L}^{-1}$	0.22	44.42	1370.00	79.7	649	30.0	34%
Total Alkalinity	mg L^{-1}	1.8	28.2	127.5	19.0	474	20	39%
Total Kjeldahl Nitrogen	mg L^{-1}	0.0	1.1	4.2	0.55	675	-	-
Ammonia	mg L^{-1}	0.01	0.29	3.00	0.29	657	0.02	68%
Nitrate	mg L^{-1}	0.00	0.18	2.17	0.18	634	10	0%
Sulfate	mg L^{-1}	1	39	195	25.5	533	250**	0%
Turbidity	NTU	1.3	4.8	34.0	3.9	271	29***	<1%
Chlorophyll a	mg m^{-3}	0.00	11.62	118.58	13.5	267	-	-
Pheophytin a	mg m^{-3}	0.01	6.39	90.05	7.99	268	-	-

* Florida Department of Environmental Protection, Chapter 62-302.540.
** National Secondary Drinking Water Regulations (40 CFR 143).
*** National Maximum Contaminant Levels (40 CFR 141).

Table 2. Pearson (r_p) and Spearman's (r_s) partial correlation coefficients and corresponding probability levels for various parameters with chlorophyll a.

Parameter	r_p	Probability (r_p)	r_s	Probability (r_s)	n
pH	0.019	0.7660	-0.014	0.8260	250
Electrical Conductivity	0.235	0.0002	0.222	0.0005	244
Temperature	0.318	0.0001	0.345	0.0001	265
Dissolved Oxygen	-0.055	0.3840	-0.046	0.4650	255
Total P	-0.132	0.0340	-0.141	0.0230	259
Reactive P	-0.120	0.0630	-0.108	0.0940	243
TN/TP	0.170	0.0120	0.237	0.0004	218
Chloride	0.384	0.0001	0.426	0.0001	116
Fluoride	0.179	0.1680	0.325	0.0110	62
Lead	-0.202	0.1460	-0.090	0.5230	54
Copper	-0.018	0.7970	-0.046	0.5140	208
Total Alkalinity	0.214	0.0940	0.256	0.0440	63
Total N	-0.009	0.8900	-0.057	0.3950	226
TKN	0.091	0.1510	0.136	0.0310	251
Ammonia	0.116	0.0760	0.100	0.1270	235
Nitrate-N	-0.401	0.0001	-0.311	0.0001	235
Nitrite-N	0.280	0.0001	0.203	0.0020	234
Sulfate	0.407	0.0001	0.405	0.0001	117
Turbidity	-0.116	0.0680	-0.104	0.1010	250
Pheophytin a	0.161	0.0080	0.280	0.0001	267
r_p = Pearson's partial correlation coefficient. r_s = Spearman's partial correlation coefficient.					

Table 3. Evaluation of Chlorophyll a equations using 1993 Lake Manatee data.

Chlorophyll a Equations	r^2	p	n
<u>Dillion & Rigler (1974)</u>			
log Chl a = -1.136 + 1.449 log TP	0.005	.5179	85
<u>Jones & Bachmann (1976)</u>			
log Chl a = -1.09 + 1.46 log TP	0.005	.5179	85
<u>Canfield (1983)</u>			
a) log Chl a = -0.15 + 0.744 log TP	0.005	.5179	85
b) log Chl a = -2.49 + 0.269 log TP + 1.061 log TN	0.07	.0414	62
c) log Chl a = -2.99 + 1.38 log TN	0.11	.0103	62
<u>Lake Manatee (this study)</u>			
log Chl a = -3.04 - 0.25 log NO ₃ + 0.58 log NO ₂ + 0.45 log TN/TP + 1.582 log Temp + 0.65 log EC	0.41	.0001	45