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Dissolved Organic Carbon in Some Dark Venezuelan Waters and a Revised Equation for Spectrophotometric Determination of Dissolved Organic Carbon

By WILLIAM M. LEWIS Jr. and DANIEL CANFIELD

With 1 figure and 1 table in the text

Abstract

The amounts of dissolved organic carbon and the absorbance spectra are given for water of the Rio Carrao and Guri Reservoir in East Venezuela. These dark tropical waters are compared with dark waters of the Southeastern U.S. by means of a revised equation that relates absorbance to dissolved organic carbon. The equation applies equally well to the tropical and temperate dark waters. This indicates that the colored compounds are qualitatively similar over a wide latitude range and can be quantitatively studied by means of simple spectrophotometry.

Introduction

The humid tropical forests of the world yield vast amounts of dark-colored water (SIOLI, 1975). These dark tropical waters are superficially similar to the dark waters of bogs and certain coastal streams and swamps within the temperate zone. The dark color in all cases is presumed to be due to refractory organic acid compounds of the type characterized by SHAPIRO (1957). In both temperate and tropical areas, the waters with large amounts of these compounds are typically poor in electrolytes and drain podzolic soils (SIOLI, 1954, 1965; KLINGE 1967).

Although dark waters are found in both tropical and temperate regions, the high yield of very dark water from such sources as the Rio Negro, Congo, and other dark tropical rivers has no equivalent in the temperate zone. The chemical properties of dark tropical waters have been studied routinely for the last two decades, beginning with the work of SIOLI and of BRAUN (1952) in tropical America. It is still unclear, however, whether the coloring compounds in the dark tropical waters are similar to or different from those of temperate dark waters. Comparison based on published data for tropical waters is difficult, as the spectral properties are

undocumented and quantitative carbon analyses of the most satisfactory type (combustion/chromatagraphy) are unavailable. A fine series of wet combustion data is available from the authors already cited and from SCHMIDT (1972, 1973), but the problem of incomplete combustion and unknown spectral properties complicates the interpretation of these data. We offer the following spectral analysis and complete combustion of samples from two dark Venezuelan waters as a preliminary basis of comparison between temperate and tropical dark waters.

Methods and Study Site

Samples were taken of the Guri Reservoir on the Caroni River and from the Carrao River at Canaima during July 1974. The drainage of both rivers is from unpopulated moist forest areas of East Venzuela (LEWIS & WEIBEZAHN, 1976). The pH, conductance, and absorbance spectra of the water samples were determined within 1 day of sampling. A gallon of water from each source was then returned in plastic to the U.S. and refrigerated several weeks prior to dissolved organic carbon (DOC) determination by combustion/chromatography (MENZEL & VACARRO, 1964). At the time of DOC analysis a second absorbance spectrum was made for each sample.

The absorbance spectrum for the fresh sample was compared with the spectrum after storage, and the two were identical for each water sample (Fig. 1).

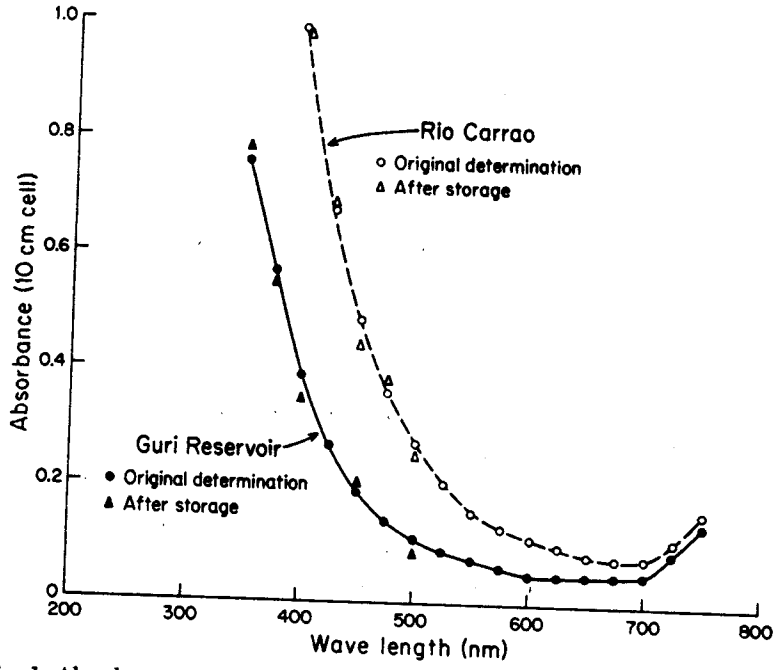

Fig. 1. Absorbance spectra of water from Rio Carrao and Guri Reservoir before and after storage.

The stability of the absorbance at short wavelengths over the storage interval indicates that the colored organic acids were unchanged in amount or quality by storage. The complete lack of change seems remarkable but is understandable in view of the sterility of the water and the refractory nature of the compounds.

The absorbance of the samples at 360 nm was used in the equation of LEWIS & TYBURCZY (1974) to compute the expected DOC.

Results

The amounts of DOC in the two water samples as determined by combustion/chromatography proved to be 5.0 mgC/l (Guri) and 11.4 mgC/l (Carrao). These results did not conform with the expected DOC based on absorbance at 360 nm. The measured values were in fact exactly half the amounts expected from absorbance. Two possibilities were considered: (1) a qualitative difference in the organic acids of the tropical waters and the waters from the Southeastern U.S. that were the basis for the equation, and (2) a uniform error in the original determinations on which the equation was based. The data records originally used in formulation of the absorbance equation were checked and a routine dilution error was discovered which caused all values to be high by a factor of exactly 2.0. Equation (1) given in LEWIS & TYBURCZY (1974) must be divided by 2.0 and thus becomes:

$$\text{DOC (mg/l)} = (1/(1394-3.32\,\lambda)) \times 10^3 \times E^{\lambda}_{10\text{ cm}} + \frac{0.45 \exp(36.4-0.121\,\lambda) + 1.24}{1 + \exp(36.4-0.121\,\lambda)} \quad (1)$$

Derivation of this equation was rechecked and proved to be sound. If the determination is made at 360 nm, as recommended by LEWIS and TYBURCZY (1974), then:

$$\text{DOC (mg/l)} = 5.03 \times E^{\lambda}_{10\text{ cm}} + 1.24. \quad (2)$$

The equation is in good general agreement with relationships noted between absorbance and DOC by other workers (MACKERETH, 1963; WETZEL and OTSUKI, 1974), but exact comparisons are difficult to make due to variation in methods and the wavelengths selected for absorbance measurements.

As insurance against analytical error, aliquots of the Guri and Carrao samples were sent to R. G. WETZEL at Kellogg Biological Station for independent DOC analysis by combustion/chromatography. WETZEL's values agree well with our values and with the predictions of the revised equation (Table 1).

Table 1. Chemical data on water samples from Guri Reservoir and the Carrao River at Canaima showing the consistency of Equation 2 from the text with combustion/chromatography analysis for DOC. Alkalinity was determined by acid titration to pH 4.4. DOC values are means for 4 or more replicates.

	Conductance μmho/cm 25 °C	pH	Alkalinity mg/l as CO_2	Dissolved Organic Carbon (mg/l) Combustion/ Chromatography	Combustion/ Chromatography (Wetzel)	Predicted (Equation 2)
Guri Reservoir	9.0	6.40	3.2	5.0	5.4	4.9
Carrao River	10.5	4.60	0.0	11.4	10.6	10.8

Conclusions

The absorbance of the dark waters from Venezuela is quantitatively indistinguishable from that of dark waters draining podzols in the Southeastern U.S. For this reason, a common equation based on absorbance at 360 nm predicts DOC almost as effectively as combustion/chromatography. Further study of the dark electrolyte-poor tropical waters should therefore be possible on the basis of spectrophotometry alone by use of the equation.

Spectrophotometric production of DOC will probably prove unreliable for waters containing large electrolyte concentrations, however (R. G. Wetzel, personal communication).

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Summary

Water samples taken from the Carrao River and the Guri Reservoir in Venezuela were analyzed for dissolved organic carbon by means of combustion/chromotography. Both waterbodies are dark in color and very poor in electrolytes. The relation between absorbance of light at 360 nm and amount of dissolved organic carbon was found to be the same as for some dark waters in the Southeastern U.S. that were tested in an earlier study. A simple equation predicts dissolved organic carbon from absorbance and has equal validity for the temperate and tropical dark waters. The dark tropical waters thus seem to be qualitatively similar to dark waters of the temperate zone.

Zusammenfassung

Wasserproben und Carraofluß und vom Guristausee in Venezuela wurden mittels Verbrennungschromatographie analysiert, um deren gelösten organischen

Kohlenstoffgehalt zu bestimmen. Beide Wasserkörper sind dunkelfarbig und besitzen einen geringen Elektrolytgehalt. Die Beziehung zwischen Lichtabsorption bei 360 nm und gelöstem organischen Kohlenstoffgehalt glich jener in einigen Schwarzgewässern der südöstlichen Vereinigten Staaten, die in einer früheren Untersuchung analysiert wurden. Mittels der Absorptionwerte ergibt eine Gleichung ersten Grades den gelösten organischen Kohlenstoffgehalt an, und diese ist für Gewässer der gemäßigten Zone sowohl wie für tropische Gewässer gültig. Die Schwarzgewässer der Tropen scheinen also den Schwarzgewässern der gemäßigten Zone qualitativ ähnlich zu sein.

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The addresses of the authors:

Dr. William M. Lewis, Jr., Department of E.P.O. Biology, University of Colorado, Boulder, Colorado 80309.

Daniel Canfield, Department of Animal Ecology, Iowa State University, Ames, Iowa 50010.