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INFRARED ABSORPTION STUDY OF HUMIC SUBSTANCES FROM LAKE APOPKA SEDIMENT, PLANKTON AND THE SURROUNDING DRAINAGE BASIN

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ABSTRACT: Infrared absorption spectra were run on humic substances from Lake Apopka sediment samples and compared with spectra from citrus and muck farm humic substances from sediment in the surrounding drainage basin, and also with spectra from autochthonous plankton humic substances. The 1540 cm^{-1} and 1650 cm^{-1} peaks in the plankton and lake sediment samples, in addition to other spectra similarities, indicate that plankton is the probable precursor of lake sediment humic substances. The absorption bands at 1650 cm^{-1} and 1540 cm^{-1} are thought to be due to peptide bonds in protein, with amide I absorption occurring at 1650 cm^{-1} and amide II absorption at 1540 cm^{-1} . The spectra from the muck farm soil and citrus soil differ to a greater extent from the spectrum of the lake sediment than do the plankton spectra.

LAKE sediments contain many kinds of organic compounds, but the main components of most lake sediments are the humic substances. In fact, humic substances are major components of the organic matter from marine and freshwater sediments and from soils. Some aquatic sediments may contain 70% of their organic carbon in the humic and fulvic acid fraction (Nissenbaum and Kaplan, 1972). These humic substances are formed during the decomposition of biogenic materials, and are biochemically resistant to further decomposition (Otsuki and Hanya, 1967). Humic substances in lake sediment can be both autochthonous, derived from the lake biota, and allochthonous, derived from the biota and soil of the drainage area. There are 2 principal hypotheses as to the formation of humic acid. One states that humic acid is derived from lignin; the other indicates that other substances such as carbohydrates are largely involved in the formation of humic acid (Otsuki and Hanya, 1967). According to Kononova (1966), the steps which constitute the process of formation of humic substances in soils are twofold: the decomposition of tissue components to simpler, chemically individual substances; and the synthesis of high molecular weight substances, humic substances, from these simpler substances. If this process also occurs in recent lake sediments the changes should be reflected in the infrared spectra of the sources of the humic substances prior to and during decomposition.

Bottom sediments of lakes and rivers may be regarded as soils which have developed under water-logged conditions. There are, however, a lack of suitable methods for classifying aquatic sediments according to their physical, chemical and biochemical characteristics, which are of importance as these characteristics can affect the limnology of the entire aquatic system.

In this study an attempt was made to use infrared methods as a limnological tool to evaluate characteristics of humic substances from a lake's bottom sediments and sediment from the surrounding watershed.

DESCRIPTION OF LAKE AND WATERSHED—Lake Apopka is located 24 km west of Orlando. This large (12,140 ha) and shallow lake (2 m) once was nationally known for its clear waters and good bass fishing. In recent decades, however, Lake Apopka has become hypereutrophic and is now populated by blue-green algae, floating mats of water hyacinths, shad, and brown bullheads. Both the cause and cure of Lake Apopka's water quality problems are controversial. Studies indicate that a major source of nutrients entering the lake was agricultural runoff from muck farms located on the north shore of the lake. Other sources of fertilization to the lake have been a citrus process plant discharge, a treated municipal sewage treatment plant effluent located in Winter Garden, Gourd Neck Spring, subsurface leaching, citrus soil runoff, rainfall, and recycled bottom deposits (Brezonik et al., 1978). The lake receives water from rainfall, runoff, seepage, and Gourd Neck Spring. The long hydraulic retention time for the lake (6.3 yr) indicates the lake is essentially a closed system.

Unconsolidated silt, muck, and peat cover over 90% of the lake bottom. This muck and decaying organic matter is very flocculent and ranges in depth from 0.3 to 12.3 m throughout the lake (Sheffield and Kuhrt, 1969). Table 1 summarizes results of several chemical and biological parameters that are useful in determining the water quality and trophic state of the lake (Brezonik et al., 1978). These data indicate extremely poor water quality and when they are applied to various trophic state indices (TSI), such as Carlson's (1977) TSI and Brezonik and Shannon's (1971) TSI, they indicate the lake is highly eutrophic.

Most of the soils surrounding Lake Apopka are well-drained sands suited for citrus production. The muck farm area located primarily on the north shore of the lake is below lake level and was once lake bottom. This muck farm area comprises 7,284 ha of nutrient-rich organic soil devoted entirely to row (vegetable) cropping agriculture. Because the farms are lower than the lake level, the nutrient-rich irrigation water must be periodically pumped

TABLE 1. Summary of 1977 mean annual levels of trophic parameters for Lake Apopka (from Brezonik et al., 1978).

Parameter	Inorg N(mg/L)	TN (mg/L)	TP (mg/L)	Ortho- PO ₄ -P (mg/L)	SD (m)	Chl a (mg/m ₃)	Net Primary Production (g C/m ³ -dav)
Value	0.095	3.51	0.222	0.047	0.29	33	0.14

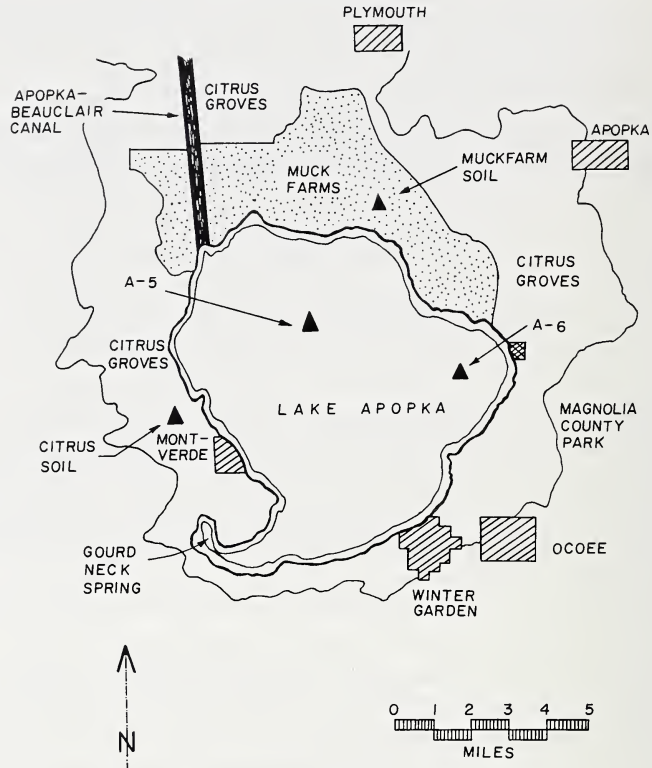


FIG. 1. Lake Apopka sampling stations and surrounding area.

into the lake. Much of the blame for the lake's rapid deterioration has been attributed to the pumpage (ECFRPC, 1973). Effective methods have presently been implemented to control nutrient inputs from the muck farms.

METHODS—Few studies of infrared spectra of humic substances from recent lake sediments have been made (Ishiwatari et al., 1965, 1966; Ishiwatari, 1967; and Otsuki and Hanya, 1967). In this study the infrared spectra of Lake Apopka sediment humic substances at various lake locations were compared with the infrared humic substance spectras of possible precursors of it, such as lake plankton, muck farm soil and citrus soil. Sample collection locations and land use types are in Fig. 1.

Samples were prepared similar to procedures outlined by Ishiwatari (1967) and Nissenbaum and Kaplan (1972). The sediment and plankton samples were dried at 105°C in an oven for 24 hr and then ground in a mortar and pestle and stored in a desiccator. The humic substances were extracted in a 0.5N NaOH solution on a shaker table for 24 hr. The humic substances were centrifuged at 9000 rpm for 20 min and the supernatant was recovered and filtered through a 0.42 μ millipore filter. The pH of the filtered solution was then adjusted to 7. The humic substances were put in semipermeable

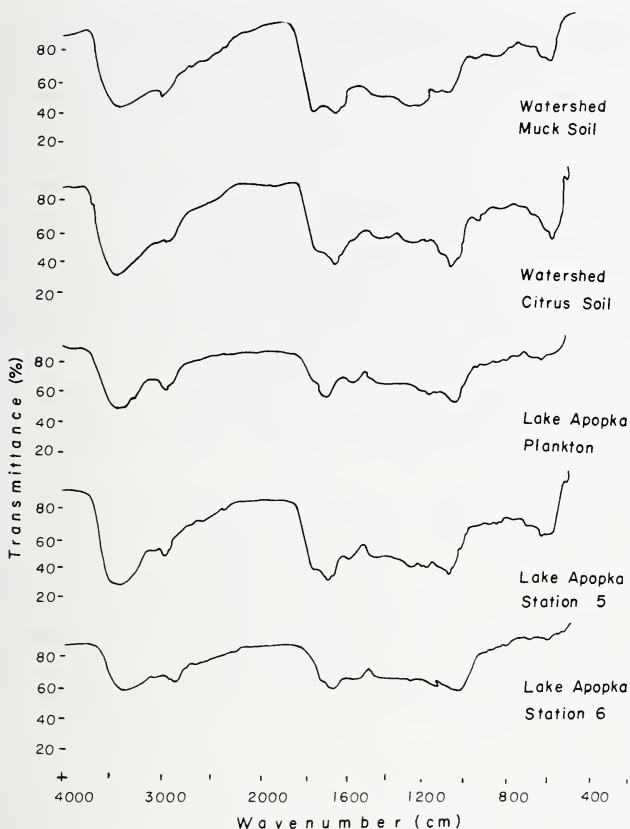


FIG. 2. Infrared spectra of humic substances from Lake Apopka bottom sediment, watershed sediment and plankton.

cellulose dialysis tubes (6.4 mm dia. pore size), and allowed to dialyze by alternating external solutions of 0.1 N NCl and distilled water for approximately 10 hr in a multiple dialyzer. This was done to purify and demineralize the sample, although part of the low molecular weight fulvic acid fraction passes through the membrane and is lost. The samples were freeze dried and then ground in a Wig-L-Bug amalgamator. The infrared spectra of humic substances and dried plankton extract were recorded on a Perkin Elmer model 127 Infrared Spectrophotometer by the common KBr disk method (ration of 300 mg KBr to 1mg sample). The infrared spectra was determined on the entire humic substance fraction and not the individual humic acid or fulvic acid fractions. Kjeldahl nitrogen determinations of the dried sediment samples were made using the standard procedure on a micro-kjeldahl apparatus.

RESULTS AND DISCUSSION—The infrared spectra are in Fig. 2. The infrared spectra of humic substances from sediment at 2 stations in the lake

differ only slightly from the plankton infrared spectrum, the main difference being that the relative intensities of the 1540 and 1650 cm^{-1} peaks are slightly greater in the plankton extract. The spectra of the citrus soil and muck farm soil differ to a greater extent from each other and from the spectra of the lake sediment and plankton samples. It has been suggested by Beer et al., (1959) that protein as a class can be distinguished with certainty from other biological compounds such as carbohydrates, lipids, or nucleic acids solely on their infrared spectra, because the variability of protein spectra is very small. The absorption bands at 1650 and 1540 cm^{-1} are thought to be due to peptide bonds in protein, with amide I absorption occurring at 1650 cm^{-1} and amide II absorption at 1540 cm^{-1} (Ishiwatari, 1967). Amide I absorption is based on the carbonyl group of a peptide bond, and amide II absorption is based on the carbon-nitrogen bond. Of significance, then, is the absence or reduced intensity of the 1540 and 1650 cm^{-1} peaks in the citrus and muck farm sediment samples.

Otsuki and Hanya (1967) suggest that humic substances in recent lake sediments are supplied from dead organisms by the action of microbes and physical-chemical alteration, but retain to a large extent the composition of the original organisms and undergo no large qualitative molecular change during decomposition. Nissenbaum and Kaplan (1972) have proven that plankton was the precursor for certain marine humic acids. In this study, the 1540 cm^{-1} and 1650 cm^{-1} peaks (protein) in both the plankton and lake sediment samples, in addition to similarities in the entire spectra of these samples, indicate that plankton is the probable precursor of the lake sediment humic substances (Fig. 2). Considering a closed lake such as Apopka, in which the high plankton production represents the major source of organic matter to the bottom, this conclusion is logical. The Kjeldahl nitrogen content of each sediment sample was determined and is in Table 2. The higher TKN content in the lake sediment and plankton samples seems to correspond to the higher protein content, as indicated by the high 1540 and 1650 cm^{-1} peaks in these samples.

The infrared absorption peaks observed from the samples are in Table 3. Major differences between the samples are that the citrus sediment has a much stronger 1040 cm^{-1} peak than the lake sediment and muck farm humic substances, indicating the strong presence of ether groups in polysac-

TABLE 2. Kjeldahl nitrogen content and percent volatile solids of sediment samples.

Station	TKN (mg N/g dry sediment)	VS (%)
Muck Farm	6.9	42.4
Citrus	1.0	2.2
A-5	23.7	59.4
A-6	21.9	66.3

TABLE 3. Interpretation of infrared absorption peaks observed in infrared spectra from Lake Apopka sediment, plankton, and drainage basin sediment.

Wave Number (cm ⁻¹)	Assignment
3400	OH groups, intermolecular bonding of hydroxy groups.
2910	Related to methylene groups, CH ₂ .
2850	Methyl groups, CH ₃ .
2325	If present, possible nitrile group, C≡N.
1720	Arises from stretching vibration of carbonyl groups of saturated aliphatic acids, ketones, or esters. Possibly from carboxylic acids in lipids.
1650	Due to amide I absorption of protein or protein-like substances, based on carbonyl group of peptide bond.
1630	C=O group of acid, ketone, or quinone.
1540	Due to amide II absorption of protein, based on carbon-nitrogen bond.
1450	Methyl and methylene group, C-H bending vibration.
1380	Methyl group, C-H bending vibration.
1220	Contribution from C-O, ether or ester. Amide III is probable.
1150	Carbon-oxygen bond.
1040	C-O stretching vibration of ether groups in polysaccharides.
920	= C-H out of plane bend, alkenes (RCH = CH ₂).

charides. The citrus humic substance also exhibited a 925 cm⁻¹ peak, which was absent in the lake sediment and muck farm samples, indicating the presence of alkenes. The muck farm humic substance had a sharper 1725 cm⁻¹ peak than the other samples, indicating a strong contribution from aliphatic acids, ketones, esters, or possibly from carboxylic acids in lipids.

This study was concerned with the characterization of sediment humic substances from Lake Apopka and its watershed. Much work remains in characterization of humic substances from other terrestrial and aquatic systems.

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POLYGONELLA POLYGAMA (POLYGONACEAE) IN FLORIDA—

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ABSTRACT: *Polygonella polygama* is considered to consist of 3 varieties of which 2, *var. polygama* and *var. brachystachya*, are found in Florida. A key to the 3 varieties and synonymy is provided. *Polygonella polygama var. brachystachya* (Meisn.) comb. et stat. nov. is proposed.

THE North American genus *Polygonella* ranges from southeastern Canada west to eastern Minnesota and south to New Mexico and Florida. Its greatest species diversity is in the southeastern states and principally in Florida.

Small (1933) recognized 5 species in the genus (*P. polygama*, *P. macrophylla*, *P. brachystachya*, *P. croomii*, and *P. americana*) and placed several other species in the closely related *Thysanella*, *Dentoceras*, and *Delopyrum*.

Fernald (1937) inconsidering *P. polygama* and *P. brachystachya*, recognized them as distinct species. The former occurs in the eastern coastal plain extending to Florida and west into Texas, while the later is restricted to Florida. Fernald further considered *P. croomii* to be a narrow-leaved variant of *P. polygama* and reduced it to a variety under the latter species. Similarly he considered *P. brachystachya* to be composed of 2 entities. The peninsular Florida taxon was considered a broad-leaved variant of the typical narrow-leaved *P. brachystachya* found in south Florida. He gave varietal status to the broad-leaved variant (*P. brachystachya var. laminigera*).

Horton (1963) revised *Polygonella* and reduced Small's genera *Dentoceras* and *Delopyrum* to synonymy under *Polygonella*. *Thysanella* was reduced to subgeneric status, also under *Polygonella*. Considering *P. polygama* to be single highly variable species, he reduced *P. brachystachya*