SOUTH CAROLINA DEPARTMENT OF NATURAL RESOURCES
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COLOR IN SURFACE WATER: A WATER SUPPLY PROBLEM IN THE GRAND STRAND OF COASTAL SOUTH CAROLINA

By

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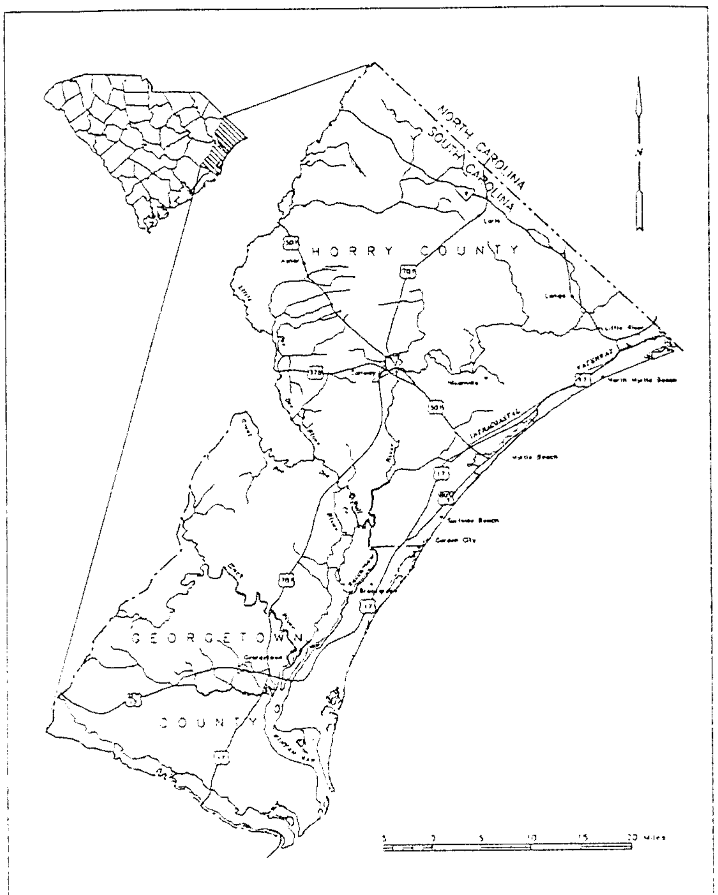
ABSTRACT

Increases in water demand along the Grand Strand in Horry and Georgetown Counties, S.C., and new water quality regulations have brought about a change in public-supply water source. The more plentiful but more expensive surface water has replaced the less abundant but less costly ground water as a source of drinking water. Today, in the Grand Strand nearly 90 percent of the drinking water comes from the Intracoastal Waterway and Bull Creek.

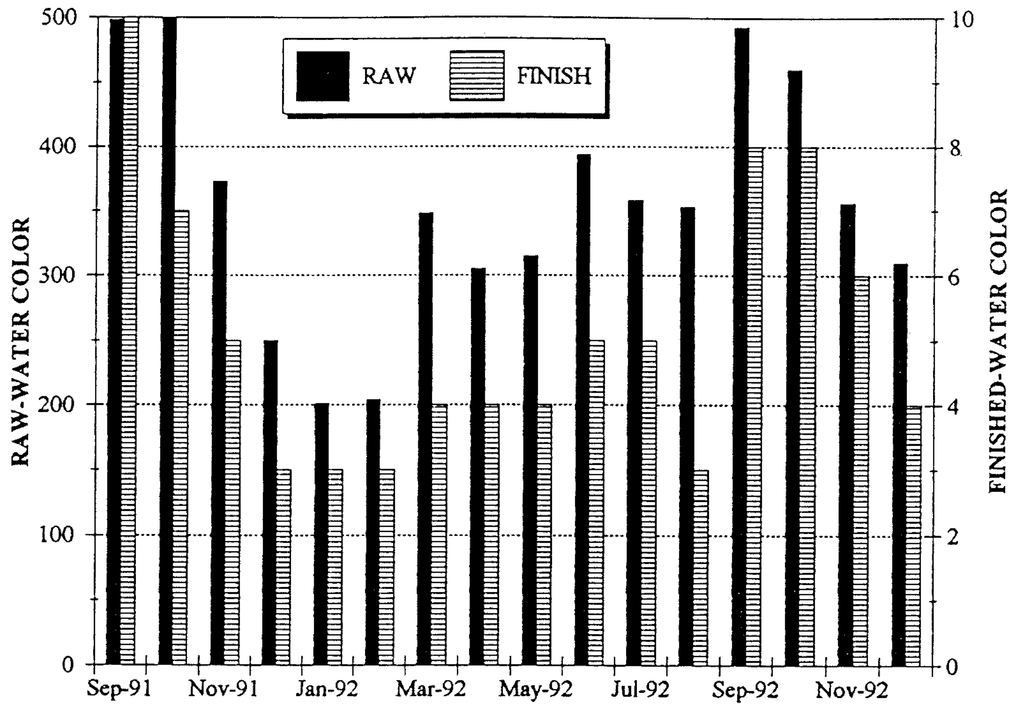
Many coastal rivers have shown periodic stages of high color, a condition known as **blackwater**. The color, although, harmless to humans, is oftentimes difficult to remove and always interferes with water-treatment processes. The color in the river water has been attributed to humic substances; it comes mostly from leached organic debris.

A better understanding of the chemical composition of the organic matter is necessary to derive more effective and less costly treatment techniques, and to ascertain their diagenesis and environmental importance.

INTRODUCTION



Extensive beaches, numerous golf courses, and a mild climate have made the Grand Strand in South Carolina a popular year-round resort. Beach-going tourists flock along coastal Horry County and northern Georgetown County from early March to late September. During the off season, October through April, golfers have made this area a favored winter retreat. Accelerated growth of the Grand Strand, in combination with stringent national water quality regulations, has forced local water utilities and municipalities to upgrade their water treatment facilities. Today, in Horry and



Color variation in the raw water and finished water at the City of Myrtle Beach treatment plant.

Georgetown Counties, surface water has replaced ground water as the major source of drinking water, reversing a 100-year practice. For these counties, the Pee Dee River, Bull Creek, and the Intracoastal Waterway presently meet most of the water needs. The development of these surface-water sources has brought about new challenges for treatment-plant managers. In coastal South Carolina, the rivers--which drain swampland--have a characteristic dark-brown color. The color, although harmless to humans, imparts to the water an unappealing appearance, interferes with water-treatment processes (disinfection), and oftentimes is not easily removed. At the raw-water intake for the City of Myrtle Beach treatment plant on the Intracoastal Waterway, color ranged from 200 to 500 units in 1992 (see graph). The intensity of the color appears to increase during the fall and decrease during the winter. Spring and summer months show higher color than winter but lower than fall. Color-treatment effectiveness varies and often is not related to color intensity, which makes color removal a difficult and costly process.

A preferred method of color removal has been oxidation, normally with chlorine (Thurman, 1985). This procedure, however, has raised the level of concern among health officials because of the formation of mutagenic byproducts. Triahalomethanes (Singer, 1989) and organic halogens (Johnson, 1983) are formed from the reaction of free chlorine and certain types of organic matter. Consequently, the organic matter, which is abundant in these coastal streams, may be a key precursor in the formation of trihalomethane and organic halogens. Thus, the understanding and characterization of the organic matter is essential in the development of better and safer treatment procedures.

Many investigations have been made to study the composition of organic matter. These investigations were directed at the carbon cycle and its role in primary productivity of plant organic matter. Few studies nationwide, and none in South Carolina, have addressed the relationship between color in surface water and organic matter as they relate to water treatment processes and water quality.

ANALYTICAL TECHNIQUES

Humic substances constitute 40 to 60 percent of dissolved organic carbon and thus are the main component of organic matter in water. These colored, polyelectrolitic, organic acids are nonvolatile and range in molecular weight from 500 to 5,000; their elemental composition is approximately 50 percent carbon, 4 to 5 percent hydrogen, 35 to 40 percent oxygen, 1 to 2 percent nitrogen, and less than 1 percent phosphorous. The major functional groups are carboxylic acids, phenolic hydroxyl, carbonyl, and hydroxyl groups.

The dissolved organic carbon in natural water probably comes mostly from leached organic debris (Thurman, 1985) and is believed to be the cause of the color in river water. The terms **humic** and **fulvic** acids are frequently used when referring to this colored water. Humic acid, for example, is defined as the fraction of organic matter precipitated by acid, and fulvic acid as the fraction remaining in solution (Hem, 1985). These terms, however, do not define chemical compounds nor refer to chemical or biological pathways. The challenge, then, is to quantify and identify the amount of organic carbon in water and to explain its relation to color.

An important objective in studying the aquatic humic substances--understanding their structure and chemical makeup--is to determine their diagenesis and environmental importance. Thus, the aquatic humic substances must first be isolated from the natural complex system where they are found (organic and inorganic matter). Unfortunately, some of the analytical techniques used impart nonreversible changes that alter the properties of isolated material. Consequently, the choice of method requires careful consideration.

The isolation of aquatic humic substances, normally, involves (Thurman and others, 1988), (a) pretreatment (b) extraction (c) acidification and (d) purification.

A partial review of the literature between 1983 and 1996 shows that the conventional method for isolation of the organic matter has been adsorption onto XAD resins (Ertel and others, 1984; Meyers and others, 1986; Hedges and others, 1992). Recently, tangential-flow ultrafiltration, which is not chemically selective and does not require pH adjustment like the XAD, appears to be a more effective technique (Benner and others, 1991 and 1992; van Heemst, J.D.H, and others, 1993). Other techniques (Table 1) have been used to a lesser extent.

To study the structure and chemical composition of the humic substances and, in general, of the organic matter, several methodologies have been proposed. There are different ways of classifying these techniques, such as degradative and nondegradative and by the type of property that is measured (Table 2). No one technique is self sufficient, hence, a combination of them provides the best results.

Table 1. Common isolation techniques for dissolved organic carbon

METHOD	COMMENTS
Coprecipitation (ferric-chloride)	slow and tedious
Electrolysis	
Liquid extraction	effective for color removal
Carbon adsorption	difficult to elute dissolved carbon
Ion exchange	
Freeze-concentration	concentrates inorganic carbon
Freeze-drying and roto-evaporation	concentrates inorganic carbon
Ultrafiltration	

The chemical composition of the organic matter has been mostly elucidated by gas chromatography/mass spectrometry (GC-MS) and nuclear magnetic resonance (NMR). In the GC-MS approach, which simultaneously can separate, identify, and quantify, inferences are made on the basis of the identity and yields of degradation products. Hedges and his coworkers, at the University of Washington, have successfully used this technique in a number of studies (Ertel and others, 1985; Meyers and others, 1986; Goni and Hedges, 1990a, 1990b, 1990c, 1992, 1995). Gas chromatography has also been used extensively (Hedges and others 1986 and 1988; McDowell and Likens, 1988; Richey and others, 1990; Moran and others, 1991 and 1994).

In the NMR (nondegradative) approach, humic substances are analyzed directly without further chemical alteration. Advances in crosspolarization/magic-angle spinning (CP/MAS) instrumentation (Norwood, 1988) have made the NMR the most promising technique. Several studies used NMR to characterize the marine organic matter (Gillam and Wilson, 1985; Benner and others, 1991 and 1992; Hedges and others, 1992).

Table 2. Methods for characterizing humic substances

TYPE OF ANALYSIS	TECHNIQUE	COMMENTS
Elemental	C,H,C/H,O,N,C/N,S,P	Gives elemental composition of humic substances
Functional Group	Carboxyl group phenolic hydroxyl hydroxyl group carbonyl group	Related to aquatic environment
Molecular Weight	Small-angle-x-ray Gel chromatography Ultrafiltration Colligative properties	Determines molecular size under ideal conditions
Spectroscopy	Infrared visible and ultraviolet absorbance Nuclear magnetic resonance Fluorescence spectroscopy Mass spectrometry	NMR most often applied to structural determination
Chromatography	Adsorption Weak-base ion exch. Cation exchange Gel chromatography Paper chromatography	Separates humic substances into different fractions
Degradation	Permanganate oxidative Copper oxide/copper sulfate Chlorination Alkaline hydrolysis Periodic oxidation Sodium-amalgam reduction Hydrogenation Pyrolysis (thermal degradation)	Gives structural information by simplifying molecule to specific compound

Along the Grand Strand, the ICWW is freshwater mostly because of contributions from the Great Pee Dee and Waccamaw Rivers. The Great Pee Dee has its headwaters in the upper part of the Coastal Plain, but the Waccamaw has its headwaters in the lowlands and swamps of the lower Coastal Plain. It is the latter that imparts this river the commonly known characteristic of **blackwater.**

The chemical quality of the ICWW is, therefore, a complex function of the hydraulic conditions of the Pee Dee and Waccamaw Rivers. In general, the quality of the water in the ICWW is better and has less color when the Great Pee Dee contributes a larger fraction of flow to the ICWW. By contrast, the quality of the water in the ICWW worsens when the Waccamaw River provides the larger fraction of the flow. Consequently, the color-causing organic matter in the ICWW may have its sources in terrestrial plants from two types of environment (a) upper and middle Coastal Plain and (b) lower Coastal Plain. It is not surprising, therefore, to find that treatment processes, for example to remove color, are more effective during some months than others.

The determination and quantification of functional groups and chemical compounds present in dissolved organic matter is a complex endeavor. The composition of the dissolved organic carbon--type and amount of humic, fulvic, and hydrophilic acids and other simple compounds--is unknown; thus, it is desirable to use a combination of techniques for their isolation and identification.

A feasible methodology may be one similar to that used by Heemst and others (1993) in the characterization of marine dissolved organic matter for the North Pacific Ocean. The aqueous organic matter might be concentrated and isolated by ultrafiltration and characterized by NMR. Alternatively, analytical pyrolysis might be used in selected samples (Bracewell, J.M., and others, 1988). This technique combines degradation (thermal), separation by GC, and identification by MS. The complex pattern of products could be interpreted by reference to those of known biopolimers. Additionally, elemental analysis could be used to assess the abundance of hydrogen, carbon, oxygen, and nitrogen and to determine their atomic ratio, such as hydrogen/carbon (H/C) or carbon/nitrogen (C/N). The abundance of carbon, might be used to deduce about the environment where the carbon came from; or the ratio H/C might be used to identify aliphatic unsaturated or aromatic structures.

SUMMARY AND CONCLUSIONS

The accelerated growth along the Grand Strand in South Carolina and new national and state drinking water standards prompted water utilities, in this area, to upgrade their water systems. Most utilities changed from ground water, which is limited in supply, to the more abundant surface water as the source of public supply. These water sources, however, have periodically shown high color concentration, a condition typical of southeastern streams in the United States known as blackwater. The color, which is an aesthetic property of the water with no harmful health effects, may be difficult to remove and may interfere with other treatment processes.

The removal of color by oxidation, normally with chlorine, has the potential of forming mutagenic byproducts when free chlorine reacts with organic matter, which is the cause of color in the water. A feasible methodology to characterize the organic matter may be concentration and isolation by ultrafiltration and analysis by nuclear magnetic resonance. The complexity of this analytical work and its cost limits the applicability of this approach to research projects only. This, consequently, has left the field practitioner with no reliable field method to identify and quantify the organic matter and its potential for forming disinfection byproducts after treatment. Thus, there is a need for developing field methods to characterize the organic matter by measuring some subrogate properties.

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