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COLOR MEASUREMENT AND REFLECTANCE SPECTROSCOPY OF TOTAL SUSPENDED SOLIDS FOR REMOTE SENSING AND ENVIRONMENTAL MONITORING OF AQUATIC ECOSYSTEMS

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Civil and Environmental Engineering

by

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B.S., University of Illinois, Urbana-Champaign, 1985
M.S., Colorado State University, 1986
May 1998
DEDICATION

This dissertation is dedicated to my parents, Leslie and Lorraine Muirhead, in honor of their loving dedication to each other and their children. They are the simply the nicest two people I know.

“El universo habla mejor que el hombre.”
Jose Marti, 1891
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Finally, I end with the person who started all this during a conversation on his back porch in Fort Collins, Colorado, over ten years ago, Professor Donald Dean Adrian. Whatever meager contributions I make to the field of Environmental Engineering, they will all be born of that conversation and the thoughtful intelligence of this kind man who took an interest in a shy kid sitting in the back of the classroom. I will be forever grateful for the fact that he never gave up on me.
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ABSTRACT

Water color and water quality are related in complex and poorly understood ways. Suspended particulates, such as phytoplankton, bacteria, and soil particles, contribute significantly to the color and quality of natural water bodies by absorbing and scattering sunlight. There is currently no standard method to measure the color and optical properties of total suspended solids (TSS). Remote sensing algorithms estimate TSS concentrations from observed values of reflectance. There are spectral differences in TSS over time and space. A convenient, inexpensive, and quick method is developed and evaluated to quantify optical differences between different TSS. The technique links the traditional TSS laboratory method to the Hapke radiative transfer theory of closely packed particles. The Hapke bidirectional reflectance model is modified to incorporate the measured dry mass of TSS on the filter paper. The measured reflectances of a series of different TSS layer thicknesses (mass per filter area) enables calculation of the absorption and scattering properties of TSS particles. The specific extinction, absorption and scattering coefficients are calculated to classify TSS.
The observed relationship between reflectance and TSS mass loading rate is modeled. Model parameters are determined by nonlinear least squares. The parameters, expressed as functions of wavelength (390 to 700 nm), permit optical classification and comparison of TSS from different locations and times. The extinction, absorption, and scattering efficiencies, the volume single-scattering albedo ($w$) and the effective single-particle absorption-thickness ($espat$) are also calculated with the model. This is the first time these parameters have been measured for TSS. Reflectance spectra may also be converted to CIE XYZ tristimulus values or Munsell colors. The method is evaluated using eutrophic lake TSS, Mississippi River TSS, wastewater bacteria, and algae (Chladymonas reinhardtii). A remote sensing model is presented based on the Hapke model parameters. The method enables quantification of the packaging effect of algae. The technique is easily incorporated into any TSS analysis and has applications in sediment tracing and nonpoint source pollution, laboratory methods to measure TSS pigments (chlorophyll), remote sensing, water quality monitoring, and graphic arts.
CHAPTER 1. INTRODUCTION

Natural waters come in many different colors, colors which are being measured more frequently and in greater detail from farther and farther away. Ironically, the color of the particles contributing to water color is generally ignored. What we are measuring with greater precision from afar, has not been measured up close.

The characteristic blue of the open ocean becomes green as one moves closer to shore and nutrient inputs increase. This green color can be attributed to the higher concentrations of phytoplankton. In coastal and inland waters the colors become more complicated by the additional optical contributions of sediments and colored dissolved organic matter from terrestrial sources. In such cases, the water color approaches yellow-brown or even red in iron-rich watersheds or during red tides of harmful algal blooms. Hence, the color of natural waters covers the entire visible spectrum, from blue to green to red.

Historically, humans have used the visual appearance of water to assess its drinkability. Water quality and water color are inherently linked. With the advent of satellite sensors we are no
longer limited by our eyes. We are now able to see the status of the aquatic environment on a global scale in greater and greater spectral, spatial, and temporal detail.

Viewing and understanding this marine ecosystem is important because it covers over 70 percent of the earth's surface and may account for as much carbon production as terrestrial sources. In coastal areas, this vast and continuous layer of water and suspended particles comes in the vicinity of human activities. The most biologically productive and colorful waters occur in coastal areas. In some cases, however, the nutrient inputs can overwhelm the coastal ecosystem resulting in hypoxic, "dead" zones, as in the Gulf of Mexico near Louisiana. It is in these land-water interfaces, where the most complex interactions of sediments, pollutants and colors occur. Global warming may push this interface upstream as the aquatic blanket expands, converting coastal land to total suspended solids (TSS) and bottom sediments.

In upland watersheds, human activities on agricultural fields affect the amount of soil and nutrients which enter downstream water bodies. On a larger scale, practices on Midwestern farms can affect the water quality and color of waters a thousand miles
downstream. This occurred in 1997 when the diversion of nutrient-rich Mississippi River water into Lake Ponchartrain, Louisiana, caused a colorful algal bloom ranging from green to red. Hence, the interactions between human activities and natural processes in the aquatic ecosystem produce an associated water color.

The color of water as seen from above by a human observer or remote sensor is the result of the radiometrical (scattering and absorption) properties of the water molecule, dissolved constituents, and particulates. The size distinction between dissolved and particulate matter is arbitrary and is taken to be 0.7 μm in this study. Substances smaller than 0.1 μm are considered to exist as individual molecules or ions. The diameter of a water molecule is on the order of 0.0004 μm. The 0.45 micron size filter is also often used to separate dissolved and particulate substances. This dissolved-particulate threshold distinguishes the nonliving world of molecules and ions from the larger, living world of bacteria and algae. The filter retains life, passing only the lifeless, yet required, building blocks. The 0.4 μm serves as the lower limit to both life and visible light. Beyond the lower spectral limits of
our human vision, lies a lifeless world. In fact, the vast majority of aquatic microorganisms are larger than 0.7 µm, the upper limit of the visible spectrum (red light). Hence, to leap through the dissolved-particulate threshold of a filter, is to leap across the visible spectrum which separates the biological and chemical worlds. Just as the origins of life on Earth are often traced to light and water, we find that color and aquatic life are linked by their size.

The optical properties of pure water (which give the open ocean its characteristic blue hue) are well known and documented. Ions associated with seawater do not significantly alter the optical properties of water. For dissolved constituents, the major contributor to water color is colored dissolved organic matter (CDOM), also called aquatic humic substances, yellow substance, or gelbstoff. Most CDOM in coastal waters originates from soils, particularly anaerobic soils. The optical contribution of CDOM is easily quantified by measuring the absorbance (absorbance relative to pure water) spectrum of a filtered water sample (CDOM does not scatter visible light). CDOM exhibits a characteristic
exponential curve (Moore, 1985) with increased absorbance in the shorter wavelengths (ultraviolet and blue).

The most significant and variable contributor to water color is total suspended solids. These particles, with diameters greater than 0.7 µm, strongly affect the fate of light radiation in water by scattering (changing direction) and absorbing (capturing) photons. Scattering due to particles is a very complex process because it is directional (3 dimensional) and depends on the concentration, size, shape, and refractive index of the suspended material. Multiple scattering may also occur, in which a single photon may interact with several water constituents being scattered in a different direction over and over each time it interacts with a scattering particle. Moreover, the particulate population is not a homogeneous group, but rather, a diverse mixture of countless organic and inorganic materials with unique absorbing and scattering properties.

Despite their small size, TSS in the form of algae and other photoautotrophic microorganisms, are global players in the carbon cycle converting light energy into chemical energy and biomass. In addition, TSS are a major vehicle in reshaping the land and
seascapes of the Earth. TSS play a major role in nonpoint source (NPS) pollution. Nationally, agriculture is the predominant source of NPS pollution and the primary pollutant in agricultural runoff is sediment (Gomez, 1995). Environmental agencies are interested in the difficult task of tracing the sources of TSS in water bodies, especially those bodies which do not meet a designated use. The quantity and color of TSS is the result of hydrological and biogeochemical processes which depend on the nutrient status, light availability, and sediment input of the aquatic ecosystem. Hence, total suspended solids, which blanket the majority of the Earth, also come in many different colors, colors which are seldom measured and generally ignored.

Remotely sensed images are based on the reflection of sunlight from the water. It is the upwardly reflected radiation which is measured by a downward looking sensor. Light radiation can be reflected from a surface of the water specularly (mirror-like) or it can penetrate the surface and enter the water column. Most of these photons, which have travelled over 90 million miles, end their eight minute journey in the water column. Many of these photons are ultimately absorbed by pigments. The depth to which
a photon penetrates the water column is largely dependent on its wavelength and the quantity and type of TSS present. This depth may vary from a matter of centimeters for turbid river waters to over a 100 meters in clear, nutrient-poor ocean waters. Below this depth the water column is literally in the dark.

In the photic zone, aquatic life is “woven” out of photons through photosynthesis as the end of the photon’s journey gives birth to algae and the carbon cycle. At a maximal efficiency of 18% (conversion of light energy to chemical energy in the form of biomass) it takes over $4(10^{24})$ photons to convert a mole of carbon dioxide to its carbohydrate equivalent (Kirk, 1983). Hence, the relatively thin and colorful, floating blanket of aquatic life is woven from extremely fine and massless threads imported from a source millions of miles away. The upwardly directed flux of photons, swimming at the speed of 124,000 miles per second, is the result of scattering (backscattering) by water molecules and particulate matter. A portion of the upward propagating photons makes it up to the water surface and is transmitted upward back into the sky. It is these photons, now flying at 186,000 miles per second in the air, which are absorbed by color sensors in the eye.
(rhodopsin, a natural pigment) or on a satellite. To admire the color of a lake, is to end the journey of a photon.

Images of water bodies are often used to estimate the total suspended solids concentration in the water. Remote sensing is based on reflectance, which is generally defined as the ratio of upward, water-leaving radiation to downward irradiance. Traditionally, an empirical regression has sufficed to model the relationship between reflectance values and TSS concentrations for a given watershed and time. Heretofore, TSS have been quantified solely on a mass per volume basis. The reflectance, R, versus TSS relationship (generally in the red to near infrared region) has been modelled successfully using linear, log-linear, or log-log equations (Stumpf, 1992). Because different aquatic systems have different optical characteristics, the empirical models are not universally applicable to other water bodies, nor even to the same area at different times. Due to spectral variability in TSS over time and different watersheds, Stumpf and Pennock (1989) developed a quasi-theoretical model to incorporate spectral properties of the suspended sediments.
The importance of water color in global ecological processes led to the Coastal Zone Color Scanner (CZCS) on board the Nimbus 7 satellite launched by NASA to provide spatial images of the distribution of phytoplankton pigments from 1978 to 1986. Although the CZCS ceased operation several years ago, the drought in ocean color data is about to end. Several improved ocean color sensors are being launched by numerous nations. OCTS was launched in August 1996, SeaWIFS was launched in August 1997, MODIS in 1998, and MERIS (Medium Resolution Imaging Spectrometer) in 1999. In the next seven years, over 50 commercial satellites are scheduled to be launched (Shipman, 1997). These improved color sensors utilizing additional and narrower band widths are well suited for coastal areas and will increase the need for groundtruthing and optical classification of water constituents.

The purpose of this dissertation is to introduce a simple, low-cost method for rapidly measuring the visible reflectance and color of total suspended solids. Reflectance spectra are converted to absorption and scattering coefficients by linking radiative transfer theory to the typical total suspended solids analysis. Optical
coefficients can be expressed in terms of mass of sediment (specific coefficients) or depth of water sample. Values of coefficients are determined by using nonlinear curve fitting of the radiative transfer equation. The coefficients represent absorption and scattering of dried, tightly packed sediment particles on a filter paper based on reflectance measurements. The reflectance spectra are also converted to tristimulus color coordinates and may be assigned a Munsell color. The new optical attributes enable inexpensive, rapid, and rigorous quantification of spectral differences between suspended solids from all water sources. The new technique has applications in public education, graphic arts, aquatic ecology, soil science, sediment tracing and transport studies, environmental engineering, environmental monitoring, management and assessment of water quality, laboratory techniques to measure pigments (chlorophyll), remote sensing, and bio-optical models. The convenient optical characterization of TSS, which provides a new and colorful look at TSS, is the main contribution of this work. The new technique provides a useful tool for improving our understanding of water color and its relationship to water quality.
This dissertation is arranged in journal format, in which each chapter is a complete document. Chapter 2 is a literature review of related research. Chapter 3 is the laboratory method for measuring the reflectance and color of TSS and will be submitted to the *Journal of Water Environment Federation*. Chapter 4 is a comparison of two instruments for measuring TSS color and will be submitted as a technical note to *Remote Sensing of the Environment*. Chapter 5 presents the theoretical basis for the new technique which links radiative transfer theory of Kubelka and Munk to TSS analysis. Chapter 6 links radiative transfer theory of Hapke (1981, 1993) to total suspended solids analysis and will be submitted to the *Journal of Limnology and Oceanography*. Chapter 7 is a remote sensing model based on the new technique and will be submitted to the *International Journal for Remote Sensing*. Chapter 8 summarizes science and engineering applications and recommendations. Conclusions are presented in Chapter 9 and references from all chapters are grouped together in Literature Cited.
CHAPTER 2. THE COLOR OF WATER AND TOTAL SUSPENDED SOLIDS: A REVIEW

This Dissertation introduces a new method for optically characterizing total suspended solids (TSS) based on simple reflectance measurements, which are converted to optical parameters by applying radiative transfer theory to the closely packed TSS particles of known mass on a filter paper. This literature review covers the pertinent theory and applications of reflectance spectroscopy. Special emphasis is given to the scattering and absorption properties of aquatic particulates. Radiation-particle interactions are considered in both air and water. The role of total suspended solids in water quality and water color is also reviewed. Relevant research of filter pad techniques, tank experiments, remote sensing models, and color science is also discussed with respect to total suspended solids.

Total Suspended Solids and Water Quality

Total suspended solids (TSS), also called seston, is an important water quality parameter. The sources, fate, and transport of TSS in the aquatic ecosystem are of global importance. Sources of TSS are
diverse and range from distant upstream soils to algal production within the water column. Resuspended bottom sediments are also a source of TSS in shallow water bodies on windy days or flood events. The environmental status of a water body is often defined in terms of the quantity of suspended particles. TSS also play a major role in nonpoint source (NPS) pollution. Nationally, agriculture is the predominant source of NPS pollution and the primary pollutant in agricultural runoff is sediment (Gomez, 1995). TSS may also act as pollutant carriers of hydrophobic contaminants which become absorbed on the organic matter of soil particles.

TSS and its corresponding relationship to siltation, organic enrichment, and hypoxia (low dissolved oxygen) is of major concern in Louisiana. Various nonpoint sources of sediment runoff include agriculture, silviculture (forestry), urban, and construction runoff. In 1991, suspended sediments ranked 5th out of eighteen causes for major impacts on Louisiana's lakes not fully supporting designated uses (LDEQ, 1992). In the case of rivers, suspended sediments were the third major cause of nonattainment of designated uses, behind pathogen indicators and nutrients. Suspended sediment concentrations had a major negative impact
on 7000 acres of lakes and over 600 river miles in Louisiana. The major impact cause, organic enrichment leading to low dissolved oxygen, often relates to sediment color due to the dark green appearance of such nutrient rich, hypoxic waters.

TSS is a bulk parameter, which represents the dry mass of particulates per volume of water sample. The value of TSS alone gives no indication of the nature of the particles. For example, the TSS value of two entirely different waters may be identical. Hence, the same TSS value of 50 mg/L could be obtained for a river water sample (containing principally inorganic soil particles) or a eutrophic lake water sample (containing principally algae).

TSS Defined

TSS is defined based on an arbitrary particle size and drying temperature. Particulates are generally defined based on the filter pore size diameter, usually 0.1 to 1.0 μm. Glass fiber filters are used for most environmental and remote sensing applications. The smallest pore size currently available for glass fiber filters is 0.7 μm (e.g., Whatman GF/F). Substances larger than this size are retained on the filter pad and considered solids. Smaller constituents, which pass through the filter paper, are considered to...
be dissolved and existing as individual molecules or ions. There is also the possibility that viruses, clay particles, and small bacteria will pass through a 0.7 μm filter. Aquatic solids may also be separated from dissolved substances by centrifuging.

Following filtration of a known volume of water sample, filter papers containing the retained particles are placed in ovens for a specified time, usually 1 hour. Filters are then removed from the oven, placed in desiccators, allowed to come to room temperature and weighed on an analytical balance with a precision of 0.0001 g. Solids are described based on their dry (dried at 60 to 105 °C) mass per volume of water sample and defined as Total Suspended Solids (TSS). Other terms used for TSS are Total Suspended Matter (TSM), Suspended Sediment Concentration (SSC), and seston.

The value of TSS is not very sensitive to the exact drying temperature used. A typical oven temperature of 75 °C, does not give significantly different results (TSS values) from a sample stored for a long time in a desiccator at 20 °C (room temperature) (Strickland and Parsons, 1968). The role of the oven is to simply speed up the drying process. The experimental procedure for measuring TSS is given in Standard Methods for the Examination of
Water and Wastewater (Greenberg et al., 1992) and in Strickland and Parsons (1968). Environmental engineers tend to refer to Greenberg et al. (1992), whereas Oceanographers and Marine Scientists use Strickland and Parsons (1968).

The dried mass (TSS) approach tends to give a larger ‘weight’ to dense inorganic particles than to organic components. For example, the specific gravity of quartz and clays is about 2.7, whereas, the specific gravity of organic matter is closer to 1. In some cases, volatile (organic) and nonvolatile (inorganic) solids are distinguished by measuring the mass before and after ignition at 500 °C. The volatile fraction, in mg/L, is defined as TVSS (total volatile suspended solids) and the nonvolatile fraction is called fixed suspended solids (FSS). TVSS and FSS combine to equal TSS.

TSS and Water Color

Other physical and optical properties of the particles, such as their color, light attenuation, transparency, opaqueness, size, shape, refractive index, and volume are generally not measured. Relative to the relatively constant values of CDOM, TSS is the most significant and variable contributor to natural water color (Kirk, 1983). Despite this fact, there is currently no standard method or
protocol for measuring the color of TSS. The quantity and color of TSS is the result of hydrological and biogeochemical processes which depend on the nutrient status and sediment input of the aquatic ecosystem. Hence, total suspended solids in natural waters come in many different colors, colors which are seldom measured and usually ignored.

Interactions of Light Radiation and Matter

A complete and universal theory of light has yet to be developed. Albert Einstein received his only Nobel prize for his discovery of the photoelectric law (rather than his theory of relativity), a quantum theory which explains how light and matter interact, the photoelectric effect. This theory is based on Bohr's idea that electrons "occupy rungs on a ladder of energy and jump among them as photons are absorbed and emitted" (Perkowski, 1996). Einstein considered incoming light as a multitude of photons, each passing its energy on to a single electron. Despite his expertise in the field of optics, Einstein commented that he would "reflect on what light is" for the rest of his life and that his struggles with the dual nature of light (wave-particle) "might drive
him to the madhouse” (Perkowitz, 1996). The thought-provoking, dual nature of light led to the development of quantum theory.

Hence, light behaves as waves and particles (Einstein and Infeld, 1938). In the wave theory of light, light behaves as a wave with an associated velocity and wavelength. Different wavelengths correspond to different colors. The quantum theory of light describes light as “packets of energy” defined as photons. The dual nature of light is conveyed by assigning wave attributes to photons. To summarize, light is a wave when it travels through empty space, but it becomes particles of energy (photons) when it encounters a solid.

Electromagnetic energy is quantified in terms of quanta or photons. Sunlight in air consists of a continuous stream of photons travelling at $3(10^8)$ m/sec. In full summer sunlight, 1 m$^2$ of the earth’s surface receives about $10^{21}$ quanta/sec (Kirk, 1983). Each of these photons has a wavelength, $\lambda$, and a frequency, $\nu$, related by

$$\lambda = \frac{c}{\nu}$$  \hspace{1cm} (1)

where $c$ is the speed of light. The speed of light is a maximum, universal value in a vacuum ($3(10^8)$ m/sec) and a constant value in other media (i.e., $2.25(10^8)$ m/sec in water).
The energy, $\varepsilon$, in a photon is given by

$$\varepsilon = h \nu = hc / \lambda$$  \hspace{1cm} (2)

where $h$ is Planck's constant which has the value $6.63 \times 10^{-34}$ J sec.

Planck's constant, one of the smallest constants in nature, represents the number by which the frequency of vibration must be multiplied to give the least unit of energy. Planck's constant enables us to link light and energy. The energy in Joules of a photon is given by

$$\varepsilon = 1.988 \times 10^{16} / \lambda.$$  \hspace{1cm} (3)

Equation 3 enables us to convert quanta (photons) to energy and work. Monochromatic radiation flux, $\Phi$, expressed in watts (W) can be converted to quanta/sec using (Kirk, 1983)

$$\text{quanta/sec} = 5.03 \times 10^{15} \Phi \lambda$$  \hspace{1cm} (4)

Refractive Index

Because light is conceived as waves of electricity and magnetism, it travels at speeds in a medium set by the electromagnetic properties of that medium. The refractive index numerically quantifies these properties. As noted above, light travels the fastest in a vacuum. In other media its velocity is reduced. The velocity of light in the medium of interest, $c_m$, is equal
to the velocity of light in a vacuum divided by the refractive index of the medium, \( n_m \).

\[
c_m = \frac{c}{n_m}
\]  

(5)

The refractive index of a medium is a function of wavelength. The refractive index of air is 1.00028 (Kirk, 1983). In natural waters, the refractive index varies very little with temperature, salinity, and wavelength, and is generally taken as a constant, 1.33. The refractive index of very strong sugar solutions varies from 1.38 for a 30% solution to 1.49 for an 80% solution (Halliday and Resnick, 1981).

It is the rapid changes in velocity which cause bending of light (refraction) at interfaces between two media of different refractive indices. There is basically a “pileup” or “traffic jam” of light radiation at the entrance to a medium of higher refractive index (reduced “speed limit”). The wave crests of light bend at the interface where the speed changes. Since the light rays travel at right angles to the line of crests, the rays also abruptly change direction at the interface. The degree of this bending, which depends on the relative speed change, will be discussed in a more theoretical way in a subsequent section. For now, we note that the
speed limits are controlled by the electromagnetic properties of the light ("vehicles") and the electromagnetic properties of the media ("highway").

If the refractive index varies with wavelength, as it does in glass, different colors will be bent differently. The speed of red light is greater than blue light in glass. Hence, red light is bent to a lesser extent than blue light. This differential bending was observed by Newton in the form of the color spectrum.

Interactions of Light and Water Constituents

Light in natural water bodies is absorbed by four principal components: the water itself, the dissolved "yellow substance" (also known as gelbstoff, gilvin, humic substances), the phytoplankton, and the non-living particulates (tripton). Absorption by the first three constituents is fairly well documented. The contribution of water is virtually constant in all aquatic environments, as it is only weakly dependent on temperature and pressure (Jerlov and Nielsen, 1974). Absorption coefficients have been determined by Sullivan (1963), Tyler et al. (1972), and Morel and Prieur (1977). The contribution of dissolved yellow substance is not constant in all waters, but it can be determined for a given water by simply

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measuring the absorption spectrum of a filtered sample of the water (Kirk, 1976). In the case of the third component, phytoplankton, absorption coefficients have been measured for pure algal cultures (Yentsch, 1959) and some natural populations (Yentsch, 1960). Burt (1958) obtained attenuation (scattering plus absorption) spectra for nonliving particulates in the Pacific ocean. He measured attenuation of the water before and after filtering. The attenuation spectrum was mainly due to scattering, but the spectrum showed a distinct rise with decreasing wavelength which may be attributed in part to absorption by the tripton fraction at the blue end of the spectrum. Kirk (1980) measured absorption of tripton in the visible region, and concluded that it rises steadily with decreasing wavelength due to the presence of humic materials, which are either bound to mineral particles or free as particles of humus. He concluded that in turbid waters, the non-living particulate fraction is a major light absorber, in addition to being the most important light scatterer.

Light Absorption by Pure Water

The absorption spectra of pure water shows that water absorbs strongly at the red end of the visible spectrum. This is actually a
tail of the intense, infrared absorption bands. These shoulders in the red region are due to higher harmonics of the hydrogen-oxygen bond vibrational absorption of the water molecule, which is centered at 3 μm (Kirk, 1992). Pure water is essentially a black body in the infrared region of the spectrum. Oligotrophic ocean waters are blue due to this strong absorption in the red (beyond 550 nm). Pure water has very little absorption in the blue and ultraviolet regions.

Light Scattering by Pure Water

Relative to particulate constituents, water contributes very little to total scattering (scattering in all directions) of natural waters. Even in the clearest ocean waters, the total scattering coefficient is due almost entirely to the presence of living and non-living particles (Kirk, 1992).

However, in the case of backscattering, the water molecule does contribute significantly relative to particles. This is because scattering by particles is concentrated in the forward direction (Spinrad et al., 1994), with only 1-2 percent occurring at angles greater than 90° (backscattered). Pure water, on the other hand, scatters equal amounts of light backward and forward (Morel,
Hence, water, which only accounts for a very small amount of total scattering, can account for a third or more of the backscattering of light. This is important in remote sensing applications, because backscattering is responsible for most of the upwelling light that exists in the ocean, some of which emerges up through the surface.

Another difference between pure water scattering and particulate scattering is that scattering by particles does not vary much with wavelength, whereas scattering by water does. Analogous to Rayleigh scattering in the atmosphere, scattering by pure water increases with the reciprocal of the fourth power of the wavelength, and so is much more intense at the blue, than at the red end of the spectrum. In fact, the blue color of clear natural waters is a result of both absorption by water in the red end of the spectrum and the more intense backscattering in the blue end of the spectrum. To summarize, in the ocean nearly all the total scattering coefficient is accounted for by suspended particles, but water itself contributes to backscattering, and hence, to the upwelling light field.
Colored Dissolved Organic Matter

In the case of true (dissolved) color, the principal constituents responsible for color are colored dissolved organic matter (CDOM). The major source of CDOM in Louisiana is soils, especially wetland and marsh soils (anaerobic environments). CDOM is a bulk parameter representing the sum of very complex, high molecular weight, organic acids. The quantity of CDOM is given by absorbance in the blue and ultraviolet regions (Grieve, 1985; Bricaud et al., 1981; Moore, 1985; Ogura and Hanya, 1968). There is a linear relationship between absorbance in the blue and ultraviolet and the concentration of dissolved organic carbon. Highly yellow or brown colored waters often indicate anaerobic conditions. Because colored dissolved organic matter is refractory, its color can be used as a hydrologic tracer (Winiarski et al., 1995; El-Rayis, 1992). As rainfall interacts with the land surface and vegetation it picks up various amounts of CDOM depending on the land type and use. Soil chemistry, hydrology, and source material affect the amount of CDOM transported to receiving waters. Stream CDOM concentrations are a function of the flow path of the water.
through the upstream soil and the adsorptive properties of the soil through which it flowed (Aiken and Cotsaris, 1995).

Waters high in humic (yellow) substances, such as those from wetlands, are unsuitable for drinking water supplies. During water treatment CDOM reacts with chlorine (and ozone) to form toxic chlorinated (oxidized) by-products (eg., trihalomethanes). Because of its importance, a new standard method has been introduced by the Standard Methods Committee of the American Public Health Association (APHA), American Water Works Association (AWWA), and the Water Environment Federation (WEF) for measuring CDOM (Eaton, 1995). The new method uses absorbance at 254 nm (ultraviolet) to quantify natural organic matter.

Yellow substances also act as pollutant carriers in aquatic environments by enhancing the transport of hydrophobic organic contaminants (Chiou et al., 1986), pesticides (Barriuso et al., 1992), and mobilizing metals such as lead, cadmium, chromium, and mercury (Aiken and Cotsaris, 1995).

Other dissolved water constituents contributing to true color are iron and some trace metals (Moore, 1985). In most natural waters, the optical influence of iron is not detectable relative to CDOM
(colored dissolved organic matter). In the ultraviolet region, nitrate and barium absorb light (Winiarski et al., 1995).

Particulate Color

The relationship between the color of aquatic particulates (> 0.7 μm) and water color is poorly understood. The color of total suspended solids (TSS) depends on the scattering and absorbance properties of the inorganic and organic particles (Muirhead et al., 1997). All particles scatter light (change its direction) due to their particle size and refractive index (Jerlov, 1976). Most of the absorbance of light comes from organic and mineral pigments (mainly iron oxides). By far, the dominant pigment is chlorophyll a which absorbs in the blue and red regions. Hence, the color of TSS is highly dependent on the status of phytoplankton, which depends on the nutrient status of the water body. In addition, certain blue-green algal species and the 4,000 different strains of red tide algae can cause serious problems by producing toxins. Phytoplankton also have a major influence on pH and dissolved oxygen levels by consuming carbon dioxide and generating oxygen. Hence, phytoplankton both affect and are affected by water quality. The oxygen, acidity, nutrient and organic enrichment status of a water
body might be inferred from the color of TSS (phytoplankton). Another organic pigment which is seldom considered and poorly understood is humus on soil particles. Humic substances (organic matter) on soil particles are black (strong absorbers in all wavelengths).

If we heat the TSS to 500 C, we can remove the organic solids and are left with the inorganic sediment. The color of inorganics depends on the upstream soils. Hence, recognizing and quantifying the inorganic color has the potential to yield information about its upstream source. The major inorganic color constituents of soils are iron oxides and hydroxides (yellow to red) and silicilic acids, kaolinites, and white calcium carbonates (Bigham and Ciolkosz, 1993). Hardly any soil is free of iron (51 g/kg Fe in the earth’s crust). In aerobic soils, iron oxides (hematite, goethite, lepidocrocite, maghemite, and ferrihydrite) are immobile compounds of low solubility that show striking colors ranging from yellow to red. The ubiquitous presence of iron leads to the coloration of most aerobic soils, particularly in their lower horizons where the yellow to red color is not masked by black organic compounds. Iron oxides include several minerals and these
minerals have different colors. The type of minerals formed depend on the soil environment. In Louisiana, the Red River alluvial soils (low in the masking black organic matter) are responsible for the unique color of the Red River.

Remote Sensing of Water Quality

The various dissolved and particulate substances present in natural waters determine their spectral properties. The possibility of characterizing water masses by means of their optical properties is of interest to oceanographers and environmental engineers. Remote sensing activities of oceanographers rely heavily on quantifying the behavior of optically active ingredients. Environmental engineers can use spectral properties to monitor wastewater ponds and lagoons.

Natural bodies of water are absorbing-scattering media. Downwelling (entering water) solar radiation is reflected and absorbed by water bodies. Constituents in the water column directly influence the reflectance properties of the water. Attenuation of radiation in water is due to absorption and scattering processes. Upwelling (leaving water) irradiance which reaches a downward looking remote sensing device gives spectral
information pertaining to the water quality. Remote sensing techniques estimate quantities of suspended sediments (Curran and Novo, 1988), organic substances (Witte et al., 1982), and plant pigments, mainly chlorophyll and pheopigments (Dierberg and Carriker, 1994).

The sun and sky radiances and the surface transmission conditions combine to provide the energy entering through the water surface (Zanefeld, 1994). Atmospheric effects on light radiation are beyond the scope of this dissertation. The fact that water is a black body in the infrared band centered at 3 μm is often utilized to estimate atmospheric effects on reflectance values at a remote sensor. Any signal received by the sensor in these infrared wavelengths must be due to atmospheric conditions, since the reflectance of the water body is zero.

Radiance emerging upwards from the earth's surface, L, consists of scattered photons (Gordon and Morel, 1983). The effect of the ocean constituents on L can be simulated adequately by placing a hypothetical lambertian reflector of albedo R just beneath the sea surface at depth, z = 0 (Gordon and Morel, 1983). A lambertian reflector is a diffuse reflector with a rough surface which reflects
uniformly in all directions (Lillesand and Kiefer, 1987). The albedo, \( R \), is the fraction of incident electromagnetic radiation that is reflected upward. Hence, the ocean color observed by a downward looking observer is physically described by the spectral values of reflectance \( R(\lambda) \) (Morel and Gordon, 1980, Gordon and Morel, 1983). Values of \( R \), which very rarely exceed 0.1, depend on the absorption coefficient, \( a \), and the backscattering coefficient, \( b_b \) (Gordon and Morel, 1983).

Reflectance, \( R \), at the water's surface is defined as

\[
R(\lambda) = \frac{E_u(\lambda)}{E_d(\lambda)} \tag{6}
\]

where \( \lambda \) is the wavelength, \( E_u \) is the upwelling irradiance and \( E_d \) is the downwelling radiance. The ocean constituents influence \( R \) through their effect on \( a \) and \( b_b \). \( a \) and \( b_b \) are linearly summable over the constituents of the ocean (Gordon and Morel, 1983). The backscattering coefficient, \( b_b \), can be linked to the volume scattering function, \( \beta \) (Gordon and Morel, 1983).

\( R(\lambda) \) varies due to the combined influences of absorption and scattering by water itself and by its contents, dissolved and particulate matter. Yellow organic substances make up the
dominant dissolved constituents influencing $R(\lambda)$ and phytoplankton and other sediments are the principal particulates affecting $R(\lambda)$ (Morel and Gordon, 1980).

It is difficult to convert color to water quality (infer content of the water from $R(\lambda)$ values) in coastal waters which have several different spectrally active constituents (CDOM, sediments, and phytoplankton). Color provides an approximate estimate of the depth of the euphotic zone (Morel and Gordon, 1980).

Above the water, the reflected light at the surface is added to and masks the signal emerging from beneath the surface. The estimate of the fraction of the signal due to reflection can be done in the near IR (740 nm) and then extended to the whole spectrum, allowing recovery of the useful marine signal by subtraction (Morel and Gordon, 1980).

Importance of relationship between water chromophores and $R$ enables use of remote sensing techniques to quantify spectrally active water constituents. Reflectance is often related to inherent properties of water, usually, the absorption coefficient, $a$, and backscattering coefficient, $b_b$. 

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By assuming that the upwelling radiance distribution from turbid water mixtures is diffuse one can relate underwater irradiance reflectance, \( \rho_u \), to the absorption, \( a \), and backscatter, \( b_b \), coefficients (Witte et al. 1982):

\[
\rho_u = C \frac{b_b}{b_b + a}
\]  

(7)

where \( C \) is a coefficient (slope of linear line). Backward scatterance is defined (Jerlov, 1976) as the ratio of the radiant flux scattered through angles \( 90^\circ (\pi/2) \) to \( 180^\circ (\pi) \) from a beam, to the incident flux.

Prieur and Morel (1977) derived a simpler relation given by

\[
\rho_u = 0.33 \frac{b_b}{a}
\]  

(8)

Hence the irradiance ratio, \( E_u(\lambda) / E_d(\lambda) \), is approximately proportional to the ratio of the back-scattering coefficient to the attenuation coefficient. It obtains a maximum value of 10 percent for blue light in the clearest water (Jerlov and Nielsen, 1974). Equation 8 indicates that remote sensing reflectance is highly backscattering dependent (Spinrad et al., 1994).
Remotely Sensed Reflectance and the Concept of an Asymptote

Researchers have presented many different models to describe the relationship between remotely sensed values of reflectance and suspended sediment concentrations. The function of $R$ versus TSS has been modeled as linear (Munday and Alfoldi, 1979), logarithmic (Stumpf, 1988), power (or log-log) (Violler and Sturm, 1984), and logistic (Munday and Alfoldi, 1979, Stumpf and Pennock, 1989). Nonlinear models give higher correlation coefficients than linear models (except for small ranges of concentration).

Quasi-Analytical, Logistic Models

Munday and Alfoldi (1979) and Stumpf and Pennock (1989) applied a radiative transfer model of a logistic form to the $R$-TSS relationship and found that the model predicted an asymptotic value. This asymptotic behavior was confirmed by Schiebe et al. (1992) and Lodhi et al. (1997). Schiebe et al. (1992) found the exponential relation to best model a 12 year long data set which covered a large range of TSS values and seasonal conditions in Lake Chicot, Arkansas. This is in contrast to other researchers who
were able to model reflectance over a single season or date (with correspondingly small range of TSS values) using linear regressions. Schiebe et al. (1992) found it difficult to separate out the differing contributions of backscatter from suspended sediments and backscatter from phytoplankton at low suspended sediment levels. They found that they had to model the relationship between R and TSS separately above and below 25 mg/L. This is because above 25 mg/L inorganic sediments dominated, whereas below 25 mg/L factors other than inorganic particulates contribute significantly to the reflectance signal (Schiebe et al., 1992). This gives an indication that the color of sediments is a function of TSS values, ranging from phytoplankton color at low TSS to inorganic color at high TSS values.

The logistic model of Stumpf and Pennock (1989) is based on the radiative transfer model developed by Gordon et al. (1975) for an optically deep and homogeneous water column. The reflectance, $R_\infty$, just above the water surface is given by:

$$R_\infty = \frac{v'b_p}{a + b_p} \quad (9)$$
where \( y' \) is a constant \( = 0.33/ (m^2 T_\infty) \); \( m \) is the refractive index of seawater and \( T_\infty \) is the transmission through the water surface. For turbid water, Equation (9) becomes (Stumpf and Pennock, 1989)

\[
R_w = \frac{y' F_s}{1 + \frac{G_s}{n_s}}
\]

(10)

where \( n_s \) is the sediment concentration; \( y' = 0.178 \); \( F_s = b_{ns}^* / s^* \); \( G_s = a_{xs} / s^* \); \( s^* = b_{ns}^* + a_{xs}^* \); \( b_{ns}^* \) is the specific backscatter coefficient for the sediment; \( a_{xs}^* \) is the specific absorption coefficient for sediment; \( a_{xs} \) is the absorption for non-sediment constituents, including water (\( a_w \)), dissolved pigments (\( a_d \)) and chlorophyll (\( a_c = a_c^* n_c \) where \( a_c^* \) is the specific absorption coefficient for chlorophyll and \( n_c \) is the chlorophyll concentration. The value of \( y' \) (0.178) accounts for transmission and reflection losses at the air-water interface. It may be noted that chlorophyll, despite being a particulate pigment, is separated from the particulates and grouped with the dissolved constituents during this approach. Coefficients (\( F_s \) and \( G_s \)) in Equation 10 are estimated with a non-linear curve fitting or through linear regression after rewriting Equation 10 into the relationship \( 1/R_w \) versus \( 1/n_s \) (Munday and Alfoldi, 1979). Stumpf (1992) reported values of \( F_s \) ranging from 0.24 (Delaware Bay) to
0.41 (Mobile Bay) and values of $G_s$ ranging from 21.0 (Mobile Bay) to 26.4 (Delaware Bay) for small, short-term data sets.

Equation 10 provides coefficients which can be interpreted in context of the materials in the water (Stumpf, 1992). Unlike regression models, this model is applicable to waters containing optically different sediments. The relationship between $R_\alpha$ and TSS may change with algal blooms or with large changes in the grain-size of the sediment. The variable $G_s$ is directly affected by pigments such as chlorophyll through $a_\alpha$, where $a_\alpha$ is linearly proportional to the concentration of pigments. Thus determinations of pigment concentrations can be incorporated into Equation (10).

Grouping the chlorophyll with the dissolved constituents creates problems as $n_\alpha$ approaches infinity, Equation 10 predicts that the reflectance value approaches the asymptote given by

$$R_{n_\alpha \to \infty} = \frac{y^* b^*_m}{a_i + b^*_m}$$

hence, the reflectance is solely a function of absorption and backscattering properties of the suspended solids and independent of dissolved constituents. An inherent assumption of Equation 10 and its respective asymptote (Equation 11) is that at very high
values of TSS the inorganic particulates dominate the reflectance signal and the chlorophyll signal is entirely ignored. Although this is reasonable for most natural bodies of water, it is not universally valid (e.g. during an algal bloom). Another important point to be considered with respect to Equation 11 is the fact that the values of $F_s$ and $G_s$ are model coefficients. They are parameters which are fitted to the data set and are not physically measured. The method described in Chapter 3 may provide a measurement technique for tightly packed TSS, the value of which serves as a 'dry' asymptote.

**Linear Models**

To develop a remote sensing model utilizing the actual, measured color spectra of TSS, it might be more appropriate to use a model which does not separate chlorophyll from the particulate optical properties. Morel and Prieur (1977) developed a linear model which calculates diffuse reflectance starting with:

$$R = 0.33 \left( \frac{b'}{a} \right) (1 + \Delta)$$

(12)

where $R$ is the reflectance just beneath the water surface, $\Delta$ is a corrective term which depends on the radiance distribution and the volume scattering function, $a$ is the absorption coefficient. $a =$
$a_w + a_y + a_p$ (for water molecules, yellow substance, and particles), and $b'$ is the backscattering coefficient: $b' = b'_p + b'_w$ (for particles and water molecules).

**Tank Reflectance Experiments**

The spectral reflectance of soils suspended in waters is a function of both quantity (TSS) and characteristics (particle size and color) of the solids. Until recently, the entire focus has been on the amount of sediment while the color of the sediment has been ignored altogether. To quantify the reflectivity differences between different soils, a few tank experiments have been conducted.

A small number of researchers have used tanks filled with known quantities and types of soils suspended in water to measure reflectance. All of these tank studies demonstrate that there are significant spectral reflectance differences between different soils. The tanks are fairly large (over 7,000 liters) and painted black to minimize bottom and side reflectance (See Figure 2.1). They are lighted from above with either an external light source or the noon sun. Homogeneous soils of known quantities are added and stirred to keep them in suspension. Soil preparation and
Figure 2.1  Typical tank reflectance setup.
addition requires a great deal of careful effort and time. Radiance is measured from above with a spectroradiometer. In all cases, the color of the soils used was reported as Munsell (Munsell Soil Charts, 1975) colors by visually matching them to color plates. Barghava and Mariam (1990) measured spectral reflectance of four different clay soils at various levels of turbidity. In the visible range, the grey soil suspension with the lowest organic content had the highest values of reflectance, whereas, the black cotton soil with the highest organic content reflected the least.

In a similar study using the same tank, Barghava and Mariam (1991) measured reflectance as a function of particle size and soil type. Reflectance increased with decreasing particle size and varied with soil type. They modeled the relationship between TSS (mg/L) and reflectance, R, using

\[ TSS = a R^n \]  

(13)

This equation was linearized and the linear form was regressed to obtain values of the coefficients for the observed data. Values of a ranged from 0.01 to 4.7 \times 10^4, values of n ranged from 3.5 to 7.6, and correlation coefficients were all greater than 0.99 at 700 nm for the five soils studied.
Barghava and Mariam (1991) also presented a more generalized equation to account for the effect of particle size

\[ TSS = (a_1 + a_2D + a_3 R)^3 \]  

(14)

where \( D \) is the geometric mean diameter (mm).

Lodhi et al. (1997) measured the reflectance of two loess soils, one silty and one clayey, suspended in water. Both soils had a distinct spectral pattern of reflectance. Reflectance increased at all wavelengths for both soils as TSS increased. The dark, higher organic clayey soil had about 10% lower values of reflectance than the lightly colored, silty suspension at very high TSS levels (above 300 mg/L) in the range 580 to 720 nm. For the clayey soil, little increase in reflectance values occurred above 300 mg/L. For the silty soil, reflectance values reached a relatively constant value beyond 600 mg/L. Thus, an asymptote apparently exists for sediment loading in surface waters, and the asymptote is different for various types of soils. Lodhi et al. (1997) concluded that the visible wavelength range of 580 to 690 nm provides the most information on the type of sediments suspended in water, whereas, the near infrared wavelength range of 714 to 880 nm is

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the optimal wavelength range \( r > 0.90 \) for determining the amount of suspended sediments.

Using the wavelengths with the best correlations to sediment loading, Lodhi et al. (1997) modeled the sediment concentration as a function of reflectance values. The regression model is a second-order polynomial (see Equation 15). This model is not physically meaningful, because for infinite values of TSS, the reflectance also approaches infinity (i.e., it does not model the asymptote revealed from the experimental data).

\[
\text{TSS (mg/L)} = a + bR + cR^2
\] (15)

Reflectance exhibits an increase with increasing suspended solids. The increase, which depends on wavelength, is linear for some soils and curvilinear for others (Bargava and Mariam, 1990). These tank experiments show that reflectance values approach an asymptotic value for each wavelength. The resulting maximum reflectance spectrum has a characteristic shape and value for each soil type.
Establishing a Relationship Between the Asymptote Spectrum of a Soil Suspension and the Color of the Dried Soil

Figure 2.2 shows a comparison of the asymptote spectrum obtained by Lodhi et al. (1997) with the spectrum of the soil colors. The spectra of the two soil colors were obtained by measuring the reflectance of the Munsell chart color corresponding to the dry soil color name. Only three wavelengths are compared in Figure 2.2 (450, 550, and 650 nm). Lodhi et al. (1997) determined the soil colors by visually matching them to Munsell soil chart color plates. For the dark soil, the spectrum of the soil suspension is parallel to the spectrum of the same soil's color. The only difference is that the spectrum of the soil suspension is darker due to the presence of water. In the case of the lighter colored silty soil, the spectral lines of the suspension and soil color are parallel from 450 to 550 nm. Between 550 nm and 650 nm the vertical distance between the two lines increases with wavelength. Hence, for lightly colored solids in water, the high amount of attenuation by the water molecule beginning around 500 to 550 nm seems to have a significant effect at longer wavelengths. This effect may be masked by dark soils suspended in water.
Figure 2.2. Tank and Munsell soil color reflectance. Data is from Lodhi et al. (1997). Points are connected for illustration purposes.
The next step is to develop a model in which the quantity of a soil, of a known color, is added to water and the resulting water color observed from above is predicted. For a suspension of solids taken from a natural body of water, the color used will be the color of the TSS and the dissolved water color will include the contributions of CDOM in addition to the water molecule.

Filter Pad Techniques

The opal glass technique was introduced by Shibata et al. (1954, 1958) to measure absorption spectra of suspensions of algae, *Chlorella pyrenoidosa*, and other microorganisms. Opal glass has one side of which has an opalescent coating to overcome the effects of scattering. Prior to 1954, all previously published spectra of microorganism suspensions suffered greatly from light scattering effects, making their spectra undecipherable. The scattering problem arises from the fact that in ordinary spectrophotometers there is always a certain distance between the sample and the light detector. Hence, the diffused light emerging from the sample in a direction not intercepted by the photocell is not detected. The method of Shibata utilizes opalescent plates to diffuse uniformly both the speculately transmitted (unaltered, parallel light, which
has passed through only the suspending medium without hitting the particulates) and scattered emergent light regardless of incident direction to improve absorbance measurements in the visible region. Therefore, Shibata et al. (1954) obtained a clear absorption spectrum of microorganism suspensions with an unmodified spectrophotometer just by attaching opalescent plates to cuvettes.

Kishino et al. (1985) modified the opal glass technique to measure the absorption coefficient of phytoplankton retained on glass fiber filters (Whatman GF/F). Spectral absorptance for the suspended particles of water was determined by measuring the diffuse transmittance of filters containing the wet particles. Kishino et al. (1985) placed filter papers immediately in front of multiplier tubes and used the modified spectrophotometer to measure the transmittance of light through the filter containing phytoplankton particles. Because of this design, all transmitted and most of the scattered light is collected and measured. The major portion (greater than 90 percent) of photosynthetic pigments in natural phytoplankton can be extracted in methanol. Kishino measured the transmittance of light through filters before and after extraction

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with methanol to estimate the light absorption of the phytoplankton.

Absorption within a layer of particulate material can be significantly amplified by multiple reflection within the sediment layer on a filter (Kirk, 1980). Because there are multiple reflections and scattering of light between the filter paper and the particles on the filter paper (Shibata, 1958), a correction must be applied to the values of the specific absorption coefficient of phytoplankton when using Kishino's method. If this correction factor, called the pathlength amplification factor, β, is not applied, the light absorption is overestimated because of light energy lost to multiple reflections between filter paper and particulates. This correction value will vary depending on differences in the spectrophotometer and filter paper used. For example, Kishino et al. (1985) calculated values of β to be between 2.43 and 4.71 depending on the samples used, whereas, Kiefer and SooHoo (1982) reported much larger values for their setup (6.00) which utilized stacked halves of glass fiber filters. The pathlength amplification factor is the ratio of the optical thickness of the diffusing material to its geometric thickness. It has a minimum
value of 1 for materials that do not scatter light and values >100 for thick materials that scatter light intensely (Butler, 1962 in Kiefer and SooHoo (1982)).

Interactions of Light Radiation and Closely Packed Particles in Air

The way particles and light interact, depends to a great degree on the size of the particle relative to the wavelength of the light. For particles smaller than the wavelength, scattering is inversely proportional to the fourth power of the wavelength (Rayleigh's scattering). For larger particles, the scattering becomes independent of wavelength. When the particles are larger than the incident wavelengths, the surface of the particle can be considered infinite, and the Fresnel equations quantify the nature of the reflection and transmission. These equations are functions of the refractive index of the particle. The refractive index of media contains two components, a real part, n, which is simply the ratio of the speed of light in a vacuum to the speed of light in the medium, and an imaginary component, of magnitude k, which incorporates the absorption characteristics of the medium.
In considering the fate of light interacting with particles two other major considerations are important. The first is the vehicle, or the medium, in which the particles are imbedded, this is generally either water \((n=1.33)\) or air \((n=1.0003)\). The other consideration is the spacing or concentration of the particles. For particles which are dispersed, with relatively large distances between neighboring particles, light is scattered by reflection (mirror-like), refraction (bending of light rays due to changes in refractive indices), and diffraction (the bending of light around edges). In the case of isolated spheres of any size, Mie scattering describes the scattering process, which is characterized by forward scattering due to diffraction. Mie scattering depends only on the refractive index of the sphere and its size relative to the wavelength. For very small (relative to wavelength), nonabsorbing spheres, the Mie solution reduces to the Raleigh solution. For particles which are large relative to the wavelength, scattering is in the geometric-optics region, in which scattering is the result of diffraction, surface reflection, and refraction within the sphere. A solitary particle will affect the light in an area approximately two times its projected cross-sectional area. This is due to the
diffraction of light waves around its edges. In the case of particles packed closely together, the role of diffraction becomes negligible, due to the fact that particles are surrounded by other particles and not air. Unlike dispersions of particles, in which single scattering dominates, multiple scattering becomes important in closely packed particles. In this case a photon may be scattered several times as it interacts with more than one particle. Polarization effects are ignored by assuming that the incident radiation is unpolarized and that the large, irregularly shaped particles of interest do not polarize scattered light. In this case, the reflection of a layer of particles depends on their shape, size, and refractive index. All of these fundamental properties combine to give a particular layer of particles unique absorption and scattering properties. This dissertation will show how simple reflectance measurements may be used to quantify the absorption and scattering properties of total suspended solids on a filter paper. If the particle size and shape may be measured or estimated, more fundamental properties, such as the imaginary component of the refractive index may be calculated based on reflectance spectra.
This is particularly useful for opaque particles, in which transmission techniques are difficult.

Satellite Color Sensors

The importance of water color in global ecological processes led to the Coastal Zone Color Scanner (CZCS) on board the Nimbus 7 satellite launched by NASA to provide spatial images phytoplankton pigment distribution from 1978 to 1986. Although the CZCS ceased operation several years ago, the drought in ocean color data is about to end. Several improved ocean color sensors are being launched by numerous nations. OCTS was launched in August 1996, and SeaWIFS was launched in 1997. MODIS will be launched in 1998, and MERIS (Medium Resolution Imaging Spectrometer) in 1999. These improved color sensors utilizing additional and narrower band widths are well suited for coastal areas and will increase the need for groundtruthing and optical classification of water constituents.

Color Science: CIE XYZ Tristimulus Values

Colors can be defined in terms of three numbers. Hence we can plot any color as a point in space relative to three axes. If all possible colors are plotted with respect to the same three axes, this
space is known as a color space or color model. Thus, a different set of axes forms a different color space. CIE (*Commission Internationale de l'Éclairage*) XYZ is a color space whose coordinates (tristimulus values) represent the amounts (in percent) of three imaginary additive primaries X, Y, and Z. The CIE XYZ color model is based on a mathematical model of human vision. Reflectance spectra can be converted to CIE XYZ values based on the CIE 1931 color matching function for the 2° (field of view) Standard Observer (defined as the average human observer). All tristimulus values are associated with a specific illuminant. The CIE values X, Y, and Z for a color are defined as follows (*Light Source*, 1994):

\[
X = k \int S(\lambda) \, x(\lambda) \, \beta(\lambda) \, d\lambda \\
Y = k \int S(\lambda) \, y(\lambda) \, \beta(\lambda) \, d\lambda \\
Z = k \int S(\lambda) \, z(\lambda) \, \beta(\lambda) \, d\lambda
\]

where:

\[
k = \frac{100}{\int S(\lambda) \, x(\lambda) \, d\lambda}
\]

\[\beta(\lambda) = \text{the spectral reflectance of the sample at wavelength } \lambda, S(\lambda) = \text{the relative power of the illuminant at wavelength } \lambda, \text{ and } x(\lambda), y(\lambda),\]
z(\lambda) are the color-matching functions for the CIE 1931 2° Standard Observer.

When computing tristimulus values from actual spectrophotometric measurements, the integrals are replaced by sums. Using the weighted-ordinate method for this replacement, the formulae become:

\[
X = k \sum_{\lambda = 390 \text{ nm}}^{700 \text{ nm}} S(\lambda) \cdot x(\lambda) \cdot \beta(\lambda) \Delta\lambda \tag{18a}
\]

\[
Y = k \sum_{\lambda = 390 \text{ nm}}^{700 \text{ nm}} S(\lambda) \cdot y(\lambda) \cdot \beta(\lambda) \Delta\lambda \tag{18b}
\]

\[
Z = k \sum_{\lambda = 390 \text{ nm}}^{700 \text{ nm}} S(\lambda) \cdot z(\lambda) \cdot \beta(\lambda) \Delta\lambda \tag{18c}
\]

where \(\Delta\lambda = 10\text{nm} \).

CIE xyz Chromaticity Coordinates

The CIE XYZ tristimulus values, which form a three dimensional color space, can be reduced to a plot in two dimensions by defining CIE chromaticity coordinates x, y, and z

\[
x = \frac{X}{X + Y + Z} \quad (19a)
\]

\[
y = \frac{Y}{X + Y + Z} \quad (19b)
\]

\[
z = \frac{Z}{X + Y + Z} \quad (19c)
\]

Hence, \(x + y + z = 1\), which means that any one of the three chromaticity coordinates is trivially derivable from the other two.
In other words, if two coordinates are known, the third can always be calculated. This allows plotting of chromaticity in two dimensions, resulting in the CIE xy chromaticity diagram.

Conclusions

This Chapter has reviewed the Literature related to TSS and their optical properties. The Literature reveals that there is an asymptote associated with the remotely sensed reflectance of a water containing TSS. The value of the asymptote is a function of wavelength and depends on the color and quantity of TSS. The most recent remote sensing algorithms utilize quasi-theoretical parameters which account for spectral differences in TSS. The values of these parameters, which represent specific absorption and scattering coefficients, are found by curve fitting remote reflectances to TSS values. These models, however, still group the optical contribution of chlorophyll with the dissolved constituents, a physically unrealistic assumption which ignores the packaging effect of the chloroplast and algal cell wall.
CHAPTER 3. DEVELOPMENT AND EVALUATION OF A STANDARD METHOD FOR MEASURING THE REFLECTANCE AND COLOR OF TOTAL SUSPENDED SOLIDS

Introduction

Despite the fact that the color of water sediments provides information on the ecological status of a water body and sediment sources, it is a seldom utilized characteristic. The reflectance spectra of water sediments can also be utilized to interpret remotely sensed images. There is currently no standard method for measuring the color (visible reflectance spectra) of water sediments in a strict, quantitative way. Until recently, the task of radiometrically scanning and obtaining reflectance values of isolated water sediments has been a complicated and expensive endeavor. In this study, a new instrument, traditionally used in the graphic arts field, is evaluated as a water quality monitoring tool. The reflectance spectra obtained with the new tool provide a quantitative snapshot in time and space of the complex mixture of organic and inorganic water particulates resulting from the interaction of the biogeochemical and hydrologic cycles. These
spectra can be included in traditional water quality
monitoring databases to track temporal and spatial trends.

*Standard Methods for the Examination of Water and
Wastewaters* (Greenberg et al., 1992) contains a spectro-
photometric method for the calculation of dissolved color (filtered)
and apparent color (unfiltered) of water samples. Unfortunately
the apparent color gives little information because of the problem
of scattering, which causes a loss of spectral attributes. Spectra of
particulate suspensions in cuvettes suffer greatly from light
scattering effects, making their spectra undecipherable. The
scattering problem arises because in ordinary spectrophotometers
there is always a certain distance between the sample cell and the
light detector. Hence, the diffused (reflected) light emerging from
the sample in a direction not intercepted by the photocell is not
detected. The parallel light which is detected, gives little
information on the optical properties of the particulates
themselves.

The quantity and color of water sediments provides valuable
information on the environmental condition of coastal waters. The
color of total suspended solids (TSS), an easily measurable
quantity, is seldom measured. Color of TSS indicates the physiological status of phytoplankton. The spectral signature of phytoplankton varies with nutrient availability. For example, phytoplankton absorption coefficients are a function of nitrogen availability, depending on whether nitrate or ammonium is the primary nitrogen source (Cleveland et al., 1989). Color of inorganic sediments denotes their mineral content and terrestrial origin. Quartz-rich sediments have significantly lower reflectance in the near-infrared region than clay-rich materials (Witte et al., 1982). The spectral reflectance signature of isolated water sediments is also useful in interpreting remotely sensed images of water color.

Traditionally, remote sensing and bio-optical model algorithms to estimate suspended sediments and phytoplankton have utilized chlorophyll \( a \) measurements. However, chlorophyll \( a \)-specific absorption coefficients vary greatly in water sediments due to variations in lighting conditions and pigment packaging characteristics of phytoplankton (Perry, 1994; Kishino et al., 1985). Because chlorophyll \( a \) per phytoplankton cell varies widely, the spectral properties of phytoplankton in place of chlorophyll \( a \) measurements may provide a better estimate of phytoplankton
abundance, photosynthetic efficiency and influence on remotely sensed images (Perry, 1994).

Previously, measurement of the optical properties of water sediments, has required sophisticated and expensive equipment, such as a radiometer or modified spectrophotometer. The absorbance spectra of water sediments with chlorophyll has been done by measuring the transmittance of light through filter paper containing the sediments (Kishino et al., 1985; Kishino, 1994). This transmission technique, known as the modified opal glass technique, requires modification of a spectrophotometer and requires a correction factor due to multiple reflections between the sediments and the filter paper (Shibata, 1958).

In previous techniques to decompose spectra into color groups, the contribution to absorption by the constituent groups has been estimated with characteristic or statistical spectral shapes for each group. In this paper, we present a new technique for partitioning spectra into organic and inorganic components, which does not require assumptions about the spectral shapes of the components. The proposed method is similar to reflectance techniques to determine chlorophyll content of leaves (Lichtenthaler et al.,
The instrument used is a surface colorimeter, traditionally used to monitor color of graphic arts. The new method measures reflectance of sediments using this simple low-cost instrument. Spectra are decomposed into reflectance values for known quantities of organic and inorganic sediments. Because the proposed technique is non-destructive, it is easily incorporated into the traditional standard method for measuring total suspended solids.

Several hundred water samples and their respective water sediment color spectra were acquired for coastal areas in the Barataria Bay in Louisiana during one complete year. The Barataria Bay area is undergoing severe land loss and increasing salinity levels. These coastal waters contain relatively high amounts of both organic and inorganic suspended solids.

Summary of Proposed Methodology - General Description

In this paper a new method is proposed which enables the rapid measurement of the color of water sediments. Because the method is quick, simple and nondestructive, it may be used in conjunction with the traditional Total Suspended Solids (TSS) or chlorophyll analyses, which utilize the same glass fiber filters. Color
measurement adds less than one minute to the time of TSS analysis for a single water sample.

The newly proposed method measures the color of water sediments on a filter paper. The proposed method is based on filtering a water sample to isolate the sediments in a layer on filter paper. The isolated particulates are then radiometrically scanned to measure the visible light reflectance (390 nm to 700 nm) of the sediments. If chlorophyll is of principal concern, the wavelength range can be expanded to include the near-infrared region (390 nm to 840 nm). For the filtering procedure and mass measurement, the Standard Method for TSS (Greenburg et al., 1992) is followed. In fact, the color measurement of sediments simply adds one additional step at the very end of TSS analysis.

**Sample Preparation, Collection, Preservation, and Filtration**

Analysis is begun as soon as possible because of the impracticality of preserving the sample. Aggregation and growth or biodegradation of particulates may occur with time. We store the sample at 4°C up to the time of analysis to minimize
microbiological decomposition of solids and bring it to room temperature before analysis.

Because excessive residue on the filter may form a water-entrapping or clogging crust, we limit the sample size to that yielding no more than 200 mg residue. Samples high in dissolved solids require an additional step. We thoroughly wash the sediment on the filter with deionized water to insure removal of dissolved material. Prolonged filtering times resulting from filter clogging may distort the results and produce high results owing to increased colloidal materials captured in the clogged filter.

Water samples of known volume are vacuum filtered within hours of collection through pre-ashed glass fiber filters (Whatman GF/F, 0.7 μm) and dried for one hour at 60 C. Sufficient volumes of water samples are added to saturate the entire filter paper with sediments. Since settling velocities increase with particle size, small increments of sample volume (typically 50 mL) are added to insure uniformity throughout the layer on the filter. This insures an intimate mixture and reduces the possibility that the smaller particles with the slowest settling velocity will end up on the top of the layer. The mass of sediment on the filter papers is measured.
(to the nearest 0.1 mg) and recorded in accordance with *Standard Methods for the Examination of Water and Wastewater* (Greenberg *et al.*, 1992) to quantify total suspended solids. The dried sediments are then scanned by a radiometric system which measures spectral reflectance, $R$, (in percent) from 390 nm to 700 nm. The sediments on the filter paper are then returned to the oven at 500°C for 1 hour to remove volatile (organic) compounds, dessicated, weighed, and radiometrically scanned a second time.

**Measuring Reflectance: Geometry and Collimation of Source and Detection**

To use reflectance measurements to quantify the scattering and absorption properties of total suspended solids, the geometry and collimation of the radiation source and detector must be defined. All optical measurements, such as color, depend on the nature of the spectral measurement system. Hence, values of optical parameters for a given sediment are associated with a given geometry and reflectance refers to the fraction of incident light reflected by a material in the direction of a detector. The incident and reflected light may be collimated (directional, traveling in parallel rays) or hemispherical (diffusive, oriented at all angles).
Hence, two adjectives are associated with a reflectance measurement (Nicodemus et al., 1977; Hapke, 1993). The first adjective describes the degree of collimation of the source and the second defines that of the detector. The typical adjectives are *directional, conical* and *hemispherical*. If the source and detector have the same degree of collimation, the prefix *bi-* is used with the associated degree of collimation. For example, bidirectional reflectance refers to directional-directional reflectance.

The geometry of the incident and emergent light from a surface is shown in Figure 3.1. Three angles (i, e, and g) are used to describe the geometry of bi-directional reflectance. The angle of incidence, i, and the angle of emergence, e, are with respect to a normal to the surface, N. The phase angle, g, is the angle between the source and detector as seen from the surface. In this paper, the value of i and g is 45°, and the value of e is 0°.

**Relative Values of Reflectance**

Values of reflectance are usually reported as a fraction with respect to the reflectance of a white standard with a reflectance of unity in all wavelengths. The ideal standard surface is an infinitely
Figure 3.1. Geometry of bidirectional reflectance.
thick layer of nonabsorbing, isotropic scatterers which is illuminated and viewed in the same geometry as the sample.

Data Analysis of Reflectance Spectra

**CIE XYZ Tristimulus Values**

Colors can be defined in terms of three numbers. Hence we can plot any color as a point in space relative to three axes. If all possible colors are plotted with respect to the same three axes, this space is known as a color space or color model. Thus, a different set of axes forms a different color space. CIE XYZ (*Commission Internationale de l'Eclairage*) is a color space whose coordinates (tristimulus values) represent the amounts (in percent) of three imaginary additive primaries X, Y, and Z. The CIE XYZ color model is based on a mathematical model of human vision. Reflectance spectra can be converted to CIE XYZ values based on the CIE 1931 color matching function for the 2° (field of view) Standard Observer (defined as the average human observer). All tristimulus values are associated with a specific illuminant. The CIE values X, Y, and Z for a color are defined as follows (Wyszecki and Stiles, 1982):
\[ X = k \int S(\lambda) x(\lambda) \beta(\lambda) \, d\lambda \quad (1a) \]
\[ Y = k \int S(\lambda) y(\lambda) \beta(\lambda) \, d\lambda \quad (1b) \]
\[ Z = k \int S(\lambda) z(\lambda) \beta(\lambda) \, d\lambda \quad (1c) \]

where:

\[ k = \frac{100}{\int_S(\lambda) x(\lambda) \, d\lambda} \quad (2) \]

\( \beta(\lambda) \) = the spectral reflectance of the sample at wavelength \( \lambda \) and \( S(\lambda) \) = the relative power of the illuminant at wavelength \( \lambda \). \( x(\lambda), y(\lambda), z(\lambda) \) are the color-matching functions for the CIE 1931 2° Standard Observer.

When computing tristimulus values from actual spectrophotometric measurements, the integrals are replaced by sums. Using the weighted-ordinate method for this replacement, the formulae become (\( \Delta\lambda = 10 \) nm):

\[ X = k \sum_{\lambda = 380 \text{ nm}}^{700 \text{ nm}} S(\lambda) x(\lambda) \beta(\lambda) \Delta\lambda \quad (3a) \]
\[ Y = k \sum_{\lambda = 380 \text{ nm}}^{700 \text{ nm}} S(\lambda) y(\lambda) \beta(\lambda) \Delta\lambda \quad (3b) \]
\[ Z = k \sum_{\lambda = 380 \text{ nm}}^{700 \text{ nm}} S(\lambda) z(\lambda) \beta(\lambda) \Delta\lambda \quad (3c) \]
CIE xyz Chromaticity Coordinates

The CIE XYZ tristimulus values, which form a three dimensional color space, can be reduced to a plot in two dimensions by defining CIE chromaticity coordinates $x$, $y$, and $z$

\[
x = \frac{X}{X + Y + Z} \quad (4a)
\]
\[
y = \frac{Y}{X + Y + Z} \quad (4b)
\]
\[
z = \frac{Z}{X + Y + Z} \quad (4c)
\]

Hence, $x + y + z = 1$, which means that any one of the three chromaticity coordinates is trivially derivable from the other two. In other words, if two coordinates are known, the third can always be calculated. This allows plotting of chromaticity in two dimensions, resulting in the CIE xy chromaticity diagram.

Results

The effects of mass loading and oven duration on reflectance and chromaticity values are shown in Figures 3.2, 3.3, and 3.4 for a pure culture of algae (*Chlamydomonas rheinhardtii*). Algae were selected because they are the TSS constituent with the greatest amount of organic pigments which are subject to degradation. The reflectance spectra of algae also show the greatest differences over
Figure 3.2. Reflectance and wavelength of algae for various masses on filter paper.
(Area of filter = 0.00105 sq. m)

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Figure 3.3. Values of chromaticity coordinates for algae at various mass loading rates (dried at 70 C for one hour).
Figure 3.4. Values of chromaticity coordinates for algae at 70 C with time for mass loading of 3.9 g/sq. m.
the visible wavelengths. This particular species also has a known equant (almost spherical) shape of about 5 \( \mu \text{m} \) in diameter.

Figure 3.2 shows the dependence of reflectance on mass loading rate for the visible wavelengths from 390 nm to 700 nm. The values of reflectance approach an asymptote as the sediment loading increases. In Figure 3.3 the value of \( Y \), the brightness, is very sensitive to the mass loading rate. Values of \( x \) and \( y \), which represent the hue and saturation, are not as sensitive to mass loading rate as brightness. We are basically covering the white filter paper with layers of 'paint', in this case, green algae. Hence, the observed hue does not change with increasing numbers of layers as much as the brightness of the layers. For example, the value of \( x \) increases 5 percent from the least (1.4 g/m\(^2\)) to the greatest (3.9 g/m\(^2\)) mass loading concentration, while in the same mass loading interval, the value of \( y \) increases by 13 percent, and the value of \( Y \) decreases by 44 percent.

Figure 3.4 shows the relationship of chromaticity values to duration in a dark oven at 70 C. Once again, the values of \( x \) and \( y \) are relatively constant compared to the value of \( Y \). With time, the
brightness as denoted by the value of Y increases while the values of x and y decrease slightly.

Conclusions and Recommendations

The values of reflectance are highly sensitive to the mass loading rate on the filter paper. With increasing sediment loading, the value of reflectance approaches an asymptote (a minimum) at each wavelength. The value of the asymptote corresponds to a layer sufficiently thick so that it is opaque and the white filter no longer contributes to the observed color or reflectance values. In this paper, only finite (transparent) layers were considered. A series of finite layers' reflectance spectra may be used to estimate the reflectance of an opaque layer (see Chapter 5). Brightness is the most sensitive color attribute related to degradation. It is affected greatly by exposure to light, which rapidly degrades the chlorophyll causing the underlying white filter to contribute more to the reflectance.

Because color coordinates depend upon sediment loading, one may wish to define chromaticity or reflectance values for a specific depth or volume of water sample. For example, for a given filter size, we may define a 100 mL color. In a similar and more
universal way, we could define the color of an equivalent depth of water sample, which equals the volume of water sample divided by the area of the filter paper.

Chromaticity values are easily calculated for dried TSS on a filter paper. The new attribute of color is developed for TSS. The color measurement is easily added (one additional step requiring less than a minute) to the typical TSS analysis. TSS color is proposed as a useful and quantitative monitoring tool which can be linked to water quality. Moreover, the concept of color is easily understood by the general public. Hence, the color of TSS offers a water quality monitoring and public educational tool.
The color of water sediments provides valuable information on the ecological status of natural bodies of water. Color of total suspended sediments indicates the presence of phytoplankton and natural pigments. Color of inorganic sediments denotes their mineral content and terrestrial origin. Moreover, the spectral reflectance signature of isolated water sediments is valuable in remote sensing applications.

Traditionally, remote sensing and bio-optical model algorithms to estimate suspended sediments and phytoplankton have utilized chlorophyll $a$ measurements. However, chlorophyll $a$-specific absorption coefficients vary greatly in water sediments due to variations in species, taxa, cell size, physiological conditions, lighting conditions, and pigment packaging characteristics of phytoplankton (Perry, 1994; Kishino et al., 1985). The absorbance spectra of water sediments with chlorophyll has been done by measuring the transmittance of light through filter paper.
containing the sediments (Kishino et al., 1985; Kishino, 1994). This transmission technique, known as the modified opal glass technique, requires modification of a spectrophotometer and requires a correction factor due to multiple reflections between the sediments and the filter paper (Shibata, 1958). Because chlorophyll a per phytoplankton cell varies widely, the spectral properties of phytoplankton in place of chlorophyll a measurements may provide a more robust approach in modeling and measuring phytoplankton's abundance, photosynthetic efficiency and influence on remotely sensed images (Perry, 1994). Previously, measurement of the optical properties of water sediments, has required sophisticated and expensive equipment, such as a radiometer or modified spectrophotometer.

This paper compares the performance of a low cost, simple and portable surface colorimeter (Colortron II) to a precision radiometer (Licor 1800). Various standard reflectors and natural water sediments were scanned with both systems. The bandwidth of the colorimeter is 10 nm and the bandwidth of the radiometer is 1 nm. Characteristics of the two systems are shown in Table 4.1. The hand held colorimeter, widely used in the graphic arts field, is
analyzed for its applications to remote sensing and environmental sciences.

Materials and Methods

The two instruments measured commercial reflectance standards and a wide variety of georeferenced, dried water sediments from coastal waters in Louisiana. The accuracy of the two systems was quantified by scanning known standard reflectors (*Labsphere* 12 - 99% Reflectance Standards). Water samples of known volume were vacuum filtered within hours of collection through pre-ashed glass fiber filters (*Whatman* GF/F, 0.7 μm) and dried for one hour at 60 C. Sufficient volumes of water samples were added to saturate the entire filter paper with sediments. The mass of sediment on the filter papers was measured and recorded in accordance with *Standard Methods for the Examination of Water and Wastewater* (Greenberg et al., 1992) to quantify total suspended solids. The dried sediments were then scanned by both radiometric systems.
Table 4.1. Characteristics of the two reflectance measurement systems.

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Colorimeter</th>
<th>Spectroradiometer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model name</td>
<td>Colortron II</td>
<td>Licor 1800</td>
</tr>
<tr>
<td>Cost (excluding PC)</td>
<td>$1,200</td>
<td>$20,000</td>
</tr>
<tr>
<td>Wavelength range</td>
<td>390 - 700 nm</td>
<td>370 - 840 nm</td>
</tr>
<tr>
<td>Wavelength bandwidth</td>
<td>10 nm</td>
<td>2 nm</td>
</tr>
<tr>
<td>Weight</td>
<td>1 lb</td>
<td>20 lb</td>
</tr>
<tr>
<td>Light source</td>
<td>Internal lamp</td>
<td>External lamp</td>
</tr>
<tr>
<td>Type of measurement output</td>
<td>Relative Bidirectional Reflectance (%)</td>
<td>Irradiance</td>
</tr>
<tr>
<td>Time for one measurement</td>
<td>8 sec</td>
<td>25 sec</td>
</tr>
<tr>
<td>Area of surface measured</td>
<td>3 square mm, requires relatively flat surface</td>
<td>adjustable</td>
</tr>
<tr>
<td>Required skill level of operator</td>
<td>Minimal, very simple</td>
<td>Requires careful setup and operation</td>
</tr>
<tr>
<td>Other requirements</td>
<td>Macintosh Computer or equivalent</td>
<td>Telescope and tripod, Personal Computer</td>
</tr>
</tbody>
</table>
Calibration of Instruments

Spectroradiometer - 2nm Bandwidth

The radiometer measures irradiance from a surface every 2 nm, from 370 to 790 nm. A 99% standard white reflector disk from Labsphere was scanned under a 100 Volt light source to determine the transfer function to convert irradiances to reflectance values for the given light source-detector setup. Irradiances of all other samples measured are converted to reflectance values by dividing their measured irradiance by the irradiance of the 99% standard reflector and multiplying by 0.99. Figure 4.1 shows the irradiance detected from the 99% standard reflector (the transfer function) for the light source used in reflectance measurements.

Spectrophotometer (Colorimeter) - 10 nm Bandwidth

The colorimeter outputs optical properties of a surface in terms of reflectance values every 10 nm from 390 to 700 nm. A white, calibration target standard, unique to the instrument and a black box (0% reflectance) are scanned daily to calibrate the
Figure 4.1. Irradiance of 99 percent standard reflector measured with Licor system (transfer function).
instrument. The hand held colorimeter is placed directly over the area (3 mm²) of the surface to be scanned.

Data Results

A statistical summary of the scanned reflectance standards is shown in Table 4.2. Mean values in Table 2 are averaged over all wavelengths between 390 and 700 nm. Figures 4.2 through 4.8 on the following pages show the mean and standard deviation of reflectance measurements for the two systems for standard reflectors and natural water sediments.

Reflectance Standards

The mean values of the reflectance measured by the Colortron II are closer to the values of the standard reflector values (see Figures 4.2 - 4.5 and Table 4.2). However, the Colortron II measurements show slightly greater variance than the Spectroradiometer measurements. Differences in variance, are due in part to non-uniformity of the surface being scanned. These surface variations are measured by the Colortron, but not the Licor system which has a larger field of view. A Student's t-test ($\alpha = 0.05$) shows that mean reflectance values from the two systems are significantly different (Table 4.3) at certain
Table 4.2. Comparison of mean standard reflectance values averaged over all wavelengths (390-700nm).

99% Standard Reflector (Expected Mean = 0.99)

<table>
<thead>
<tr>
<th></th>
<th>10 nm Colorimeter (n=32)</th>
<th>2 nm Spectroradiometer (n=311)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>0.998</td>
<td>1.001</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.018</td>
<td>0.0129</td>
</tr>
<tr>
<td>COV</td>
<td>1.81%</td>
<td>1.29%</td>
</tr>
<tr>
<td>Minimum Value</td>
<td>0.928</td>
<td>0.990</td>
</tr>
<tr>
<td>Maximum Value</td>
<td>1.020</td>
<td>1.044</td>
</tr>
</tbody>
</table>

50% Standard Reflector (Expected Mean = 0.50)

<table>
<thead>
<tr>
<th></th>
<th>Colorimeter</th>
<th>Spectroradiometer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>0.522</td>
<td>0.544</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.011</td>
<td>0.00689</td>
</tr>
<tr>
<td>COV</td>
<td>2.11%</td>
<td>1.26%</td>
</tr>
<tr>
<td>Minimum Value</td>
<td>0.483</td>
<td>0.538</td>
</tr>
<tr>
<td>Maximum Value</td>
<td>0.537</td>
<td>0.569</td>
</tr>
</tbody>
</table>

25% Standard Reflector (Expected Mean = 0.25)

<table>
<thead>
<tr>
<th></th>
<th>Colorimeter</th>
<th>Spectroradiometer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>0.245</td>
<td>0.259</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.00564</td>
<td>0.00219</td>
</tr>
<tr>
<td>COV</td>
<td>2.31%</td>
<td>0.84%</td>
</tr>
<tr>
<td>Minimum Value</td>
<td>0.226</td>
<td>0.257</td>
</tr>
<tr>
<td>Maximum Value</td>
<td>0.253</td>
<td>0.269</td>
</tr>
</tbody>
</table>

12% Standard Reflector (Expected Mean = 0.12)

<table>
<thead>
<tr>
<th></th>
<th>Colorimeter</th>
<th>Spectroradiometer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean</td>
<td>0.107</td>
<td>0.114</td>
</tr>
<tr>
<td>Standard Deviation</td>
<td>0.00231</td>
<td>0.00145</td>
</tr>
<tr>
<td>COV</td>
<td>2.16%</td>
<td>1.28%</td>
</tr>
<tr>
<td>Minimum Value</td>
<td>0.100</td>
<td>0.112</td>
</tr>
<tr>
<td>Maximum Value</td>
<td>0.111</td>
<td>0.120</td>
</tr>
</tbody>
</table>

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Figure 4.2. Comparison of Colortron and Licor reflectance of 99 percent standard reflector.
Figure 4.3. Colortron and Licor reflectance of 50 percent standard reflector.
Figure 4.4.  Colortron and Licor reflectance of 25 percent standard reflector.
Figure 4.5. Colortron and Licor reflectance of 12.5 percent standard reflector.
Figure 4.6. *Colortron mean reflectance values of standard reflectors.*
Figure 4.7. Standard deviation of a TSS sample measured with Colortron (10 scans).
Figure 4.8. Mean reflectance of Colortron and Licor for TSS of LSU Lakes.
Table 4.3  Results of Student's t-test at selected wavelengths for 99 percent standard reflector.

<table>
<thead>
<tr>
<th></th>
<th>390 nm</th>
<th></th>
<th>450 nm</th>
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<th>700 nm</th>
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<tr>
<td></td>
<td>Colortron</td>
<td>Licor</td>
<td>Colortron</td>
<td>Licor</td>
<td>Colortron</td>
</tr>
<tr>
<td>0.929</td>
<td>1.036</td>
<td>1.010</td>
<td>1.005</td>
<td>1.03</td>
<td>0.9844</td>
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<td>0.923</td>
<td>1.043</td>
<td>0.990</td>
<td>1.008</td>
<td>1.01</td>
<td>0.9892</td>
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<td>0.918</td>
<td>1.052</td>
<td>0.992</td>
<td>1.018</td>
<td>1.02</td>
<td>0.9980</td>
</tr>
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<td>1.000</td>
<td>1.03</td>
<td></td>
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<tr>
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<td>0.990</td>
<td>1.01</td>
<td></td>
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<td>0.997</td>
<td>1.02</td>
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<tr>
<td>0.926</td>
<td>0.992</td>
<td>1.01</td>
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<td>0.994</td>
<td>1.01</td>
<td></td>
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<td>t-test=0.00141</td>
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<tr>
<td>α=0.05 (difference)</td>
<td>α=0.05 (no difference)</td>
<td>α=0.05 (difference)</td>
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</tbody>
</table>
wavelengths for the 99% standard reflector. The mean values of reflectance are significantly different at all wavelengths for the 12% standard reflector. Hence, for darker samples, it is important to consider the instrument and calibration technique used. Reflectance values greater than 1 (Figure 4.2) may be due to an unclean standard used to calibrate the instruments or instrumental noise.

**Natural Water Sediments**

The two measurement techniques produce spectral curves with similar shapes, but the Spectroradiometer consistently measures slightly greater values of reflectance, particularly at wavelengths below 550 nm. Variance in the Colortron spectral data depends on the uniformity of the particulate matter on the filter paper.

**Conclusions**

The results demonstrate that the colorimeter has sufficient resolution (10 nm) and reproducibility to accurately measure the unique reflectance spectra of dried water sediments and their corresponding chlorophyll absorbance at 670 nm. The low cost and convenient setup of the colorimeter makes it appropriate for quickly classifying and comparing two optically different samples.
of TSS. The method requires the filtering of water samples. But the proposed method is directly and conveniently compatible with Standard Methods for chlorophyll a and Total Suspended Solids, which utilize the same filter paper. Hence, the filtered particles simply need to be scanned prior to running the appropriate analytical examination.
CHAPTER 5. APPLICATION OF KUBELKA-MUNK MODEL TO REFLECTANCE SPECTRA OF TOTAL SUSPENDED SOLIDS ON A FILTER PAPER

Introduction

The color of natural waters depends on the optical properties of water molecules, other molecules, ions, and particulate substances. The principal contributors to coastal water color (Case 2 Waters) are the water molecule, colored dissolved organic matter, and suspended solids, generally phytoplankton and inorganic sediments of terrestrial origin. Of these constituents, it is the suspended solids which cause the greatest temporal and spatial variations in remotely sensed water color. Particulates suspended in water absorb and scatter light, some of which is scattered back in the direction of a remote sensor. The resulting light field in water determines the radiation available for photosynthesis by phytoplankton.

Aquatic particulates are generally quantified in terms of their dry mass per volume of water sample. The particulates are isolated from dissolved constituents using a filter of arbitrary pore size. In some cases the extracted chlorophyll
content and volatile fraction of solids are also measured. The attribute of color of suspended solids is generally ignored.

Suspended solids isolated on filter paper have been used to determine absorption coefficients of particulates (Shibata et al. 1954; Yentsch 1957; Shibata 1958, Yentsch 1960; Kiefer and SooHoo 1982; Kishino et al. 1985; Mitchell and Kiefer 1988; Morrow et al. 1989; Kishino 1994). Generally the absorption coefficients are given in terms of depth (m$^{-1}$), (derived by dividing the volume of water sample filtered by the area of the filter) or concentration of chlorophyll (m$^{-1}$)/(mg/L). Variations in species type, pigment packaging and cell size cause variability of chlorophyll a-specific absorption coefficients for phytoplankton found in natural waters (Duysens 1956; Kirk 1983; Perry 1994).

In this paper, I present a simple reflectance spectroscopy method based on the filter pad technique in combination with the traditional suspended solids analysis, to measure the reflectance of dried solids on a filter pad. I show that measured values of reflectance can be converted to color and other optical properties by applying approximate (two-stream) radiative transfer theory (Kubelka-Munk equations) to the closely packed, dried particulates.
on a filter paper. The optical coefficients of the particulate population are described in terms of mass or depth of water sample and provide a simple, inexpensive, and rapid technique for comparing optically different suspended solids from various natural and artificial bodies of water. The scattering and absorption coefficients derived with this method represent multiple scattering of dried and densely packed particles on a filter. Nevertheless, if the coefficients are carefully interpreted, the proposed technique may help explain the scattering and absorption properties of optically different suspended solids from various bodies of water. The linking of optical properties directly to mass is well suited for quasi-theoretical remote sensing algorithms (Munday and Alfoldi 1979; Stumpf and Pennock 1989). Such models take into account the spectral variability of suspended solids by defining specific absorption and backscattering coefficients for suspended solids. This snapshot in time and space of the particulate population, provides a valuable database for the new improved satellite color sensors with more and narrower bandwidths. The results are also appropriate for bio-optical models which consider the fate of light in the presence of
phytoplankton and inorganic sediments. The absorption spectra obtained may be used to estimate pigment concentrations in both organic and inorganic sediments.

Theoretical Methodology

Consider the fate of light radiation incident on a layer of particles packed tightly on a background paper. This is a problem in which radiation is propagating in a scattering and absorbing medium. Because of the close packing of the particles, multiple scattering occurs, in which photons are not just scattered once or twice, but several times. Schuster (1905) developed the original radiative transfer theory for scattering and absorbance by particles in stellar atmospheres. Schuster was the first to consider multiple scattering by closely packed spheres. Schuster (1905) simplified the three-dimensional analysis of reflection and transmission of a layer of particulate material by breaking all radiant fluxes into only two streams, one forward through the media and one backward (resulting entirely from scattering) through the media (van de Hulst, 1980). Hence, instead of solving the full transfer equation in all directions, Schuster solves only for the stream forward (in the direction toward the unilluminated side
of the media) and the stream backward (in the direction toward the illuminated side). Kubelka and Munk (1931) applied Schuster's approach to analyze paint pigments and dyes on paper. Kubelka (1948) presented the Schuster equations in convenient and usable explicit forms to investigate surface reflectance of absorbing and scattering media. Differences between an exact solution and the approximate solution of Schuster and Kubelka-Munk is well within the limits of error of experimental methods because isotropic scattering in tightly packed media is almost completely fulfilled (Kortüm 1969).

Kubelka and Munk (1931) based their analysis on the reflection and transmission of light by a scattering and absorbing layer (Figure 5.1), in which non-absorbing particles making up the layer are assumed to perfectly diffuse light in all directions. Hence, the intensity of the reflected radiation is presumed to be angularly independent and isotropic. Diffusive reflectance from a rough surface depends to a great extent on the particulate nature of medium and assumes that the Lambert Cosine Law is valid (the remitted radiation flux is proportional to the cosine of the incident angle and to the cosine of the angle of observation). Two distinct
Figure 5.1. Elementary layer of particles.
explanations have been proposed to conceptualize diffuse reflectance of small, closely packed particles (Kortüm, 1969). For particles having diameters greater than the wavelength of the incident light, regular, mirror-like reflection at the randomly oriented faces of the particles contributes to an isotropic distribution of radiation. This concept, known as Bouguer's elementary mirror hypothesis (Bouguer, 1760) explains the diffuse reflectance process at the surface, but ignores the multiple scattering occurring from the interior of the sample. In addition to the regular reflection which is governed by the Fresnel equations, some of the radiation penetrates the sample where it undergoes multiple reflections, refractions, and diffractions, which all contribute to a diffuse flux which reemerges from the surface of the layer. If the particle diameters are of the order of the wavelength, Mie scattering occurs, in which forward scattering dominates and is not isotropic. However, it can be shown experimentally that thick layers of densely packed particles produce an isotropic scattering distribution (Kortüm 1969).

The layer, of thickness, X, is irradiated from above in the negative x direction with a diffuse, monochromatic radiation flux.
This coordinate system (Kortüm 1969) will simplify the resulting differential equations and boundary conditions. By considering a horizontal and infinitely wide layer of finite thickness, we are able to ignore horizontal fluxes and consider only vertical fluxes of radiation. Hence, light flux lost horizontally through the edges at infinity is negligible compared to vertical fluxes.

Consider the flux through an elementary layer of thickness \( dx \). This layer of media scatters and absorbs light. The vertical distance between the backing \(( x = 0, \text{ the unilluminated side})\) and the elemental layer is \( x \). The thickness of the differential layer, \( dx \), is considered small compared to the total layer thickness, \( X \). But the elementary thickness, \( dx \), is considered large compared to the diameters of the particles so that we are considering the average effect of particles and not their individual effect (Judd, 1954).

**The Pathlength Traversed by Scattered Light**

Because the layer, \( dx \), is subjected to diffuse light at all possible angles with respect to \( x \), the average pathlength of the radiation within the layer is greater than \( dx \) (Kortüm, 1969). In passing
through a scattering sample, light may traverse an optical path which is many times the sample thickness. One consequence of this increased path length is an intensification of the absorption bands of pigments in light scattering media (Butler, 1962). The mean path length of the diffuse irradiation, $d\xi$, relative to the geometrical layer thickness, $dx$ (Figure 2). For a particular angular direction, $\theta$, the mean path length of the diffuse irradiation, $d\xi$, relative to the geometrical layer thickness, $dx$, is

$$d\xi = \frac{dx}{\cos \theta} \quad (1)$$

If the angular distribution of radiation flux falling on the layer of thickness $dx$ is defined as $dI/d\theta$, the relative intensity in the direction $\theta$ is given by

$$I_\theta = \frac{1}{I_0} \frac{\partial I}{\partial \theta} d\theta \quad (2)$$

where $I_0$ is the total flux in the hemisphere. The average value of the path length of the radiation proceeding in the $1$ (downward) direction within the layer $dx$, for values of $\theta$ from $0$ to $\pi/2$ is

$$d\xi_1 = dx \int_0^{\pi/2} \frac{1}{I_0 \cos \theta} \frac{\partial I}{\partial \theta} d\theta = u dx \quad (3a)$$
Figure 5.2. Derivation of average pathlength.
Similarly, the mean pathlength in the positive J (upward) direction is

\[ d\xi_1 = dx \int_0^{\frac{\pi}{2}} \frac{1}{J_0 \cos \theta} \cdot \frac{\partial J}{\partial \theta} d\theta \cdot v \, dx \]  

(3b)

By definition, diffuse radiation has the same intensity in all directions. The angular distribution of diffuse radiation impinging on a plane is given by Kortüm (1969)

\[ \frac{\partial I}{\partial \theta} = 2I_0 \sin \theta \cos \theta \]  

(4a)

and

\[ \frac{\partial J}{\partial \theta} = 2J_0 \sin \theta \cos \theta \]  

(4b)

Hence, Equations (3a) and (3b) become

\[ u = \int_0^{\frac{\pi}{2}} 2 \sin \theta \, d\theta = 2 \]  

(5a)

\[ v = \int_0^{\frac{\pi}{2}} 2 \sin \theta \, d\theta = 2 \]  

(5b)

and, thus,

\[ d\xi_1 = 2 \, dx \]  

(6a)

\[ d\xi_2 = 2 \, dx \]  

(6b)
The mean path length of the diffuse irradiation is twice the geometrical layer thickness.

Development of Radiative Transfer Equations for Closely Packed Particles

Consider what happens to the downwelling flux, $I$, during its passage through the elemental layer. The flux is decreased due to two simultaneous phenomena, absorption and scattering (specifically backscattering). The amount of flux, decreased due to absorption is given by $k \ I \ 2dx$, where $k$ is the absorption coefficient of the media. The amount of flux, decreased due to backscattering is given by $s \ I \ 2dx$, where $s$ is the scattering coefficient of the material making up the layer. Radiance that is scattered into the forward hemisphere is assumed to be unscattered by Kubelka and Munk (1931).

Now consider the changes in flux of the upwelling (in the direction towards the illuminated side) flux, $J$, during its passage through the same elementary layer of thickness $dx$. This flux is reduced by the amounts, $k \ J \ 2dx$ and $s \ J \ 2dx$, by absorption and scattering in exactly the same way, but the part $s \ I \ 2dx$, reversed in direction by scattering from the downward-proceeding flux, is
added to the upward-proceeding flux (Judd, 1952). Any light that is scattered backwards simply adds to the flux in the opposite direction. The total change, dJ, of the upward-proceeding flux is thus:

\[ dJ = -kJ^2dx - sJ^2dx + sI^2dx \]  

(7a)

or if we define \( 2k = K \) and \( 2s = S \) then

\[ \frac{dJ}{dx} = -(K + S)J + S I \]  

(7b)

in which fluxes in the positive x direction (increasing x) are indicated by a positive algebraic sign. Similarly for the downward-proceeding flux, the total change in flux is

\[-dl = -kl^2dx - sl^2dx + sj^2dx \]  

(8a)

or

\[ -\frac{dl}{dx} = -(K + S)l + S J \]  

(8b)

From these equations it is seen that the intensity change from a vertical flux traversing dx is made up of three parts (two sinks and one source). The subtractive components (sinks) are due to absorption and backscattering, while the source is due to backscattering of the oppositely directed flux.
Solution to the Radiative Transfer Equations for Closely
Packed Particles

The solution of the above simultaneous, linear, homogeneous
differential equations (Equations (7b) and (8b)) subject to two
boundary conditions is given by Kortum (1969). The differential
equations can be written

\[- \frac{dJ}{S \, dx} = a \, l + J \]
\[\frac{dJ}{S \, dx} = -a \, J + l \]

(9)

where, a, is defined as

\[\frac{S + K}{S} = 1 + \frac{K}{S} = a \]

(10)

We define, r, such that

\[r = \frac{J}{l} \]

(11)

Divide the first equation by l, and the second by J and add the two,
yields

\[\frac{dr}{S \, dx} = r^2 - 2ar + l \]

or

\[\int_{r^2 - 2ar + l}^{dr} = S \int dx \]

(12)

Integrating Equation 12 over the entire thickness of the layer, X,
subject to two boundary conditions:
\( x = 0: \) \((J/I)_{x=0} = R_x = \text{reflectance of the background},\)

and

\( x = x: \) \((J/I)_{x=x} = R = \text{reflectance of the sample},\) yields:

\[
\ln \frac{(R - a - \sqrt{a^2 - 1})(R_x - a + \sqrt{a^2 - 1})}{(R_x - a - \sqrt{a^2 - 1})(R - a + \sqrt{a^2 - 1})} = 2S X \sqrt{a^2 - 1} \tag{13}
\]

When \( X = X_x, R = R_x, R_y = 0 \) (a layer of sufficient thickness such that no light reaches the backing)

\[
(-a - \sqrt{a^2 - 1})(R_x - a + \sqrt{a^2 - 1}) = 0 \tag{14}
\]

or solving for \( R_x, \)

\[
R_x = a - \sqrt{a^2 - 1} = 1 + \frac{K}{S} - \sqrt{\frac{K^2}{S^2} + 2 \frac{K}{S}} = \frac{S}{S + K + \sqrt{K(K + 2S)}} \tag{15}
\]

\( R_x \) is the diffusive reflectance of an infinitely thick sample. It is the reflectance of a particulate layer so thick that further increase in thickness, however great, does not significantly change its reflectance (Judd, 1952). This layer is considered as infinite in the optical sense, in that it is opaque and not transparent. \( S \) is the scattering coefficient and \( K \) is the absorption coefficient of the material. The scattering coefficient of the Kubelka-Munk theory defines scattering as radiation which is reflected backward into the
opposite hemisphere. Hence, the scattering coefficient, $S$, is defined by (Kortüm 1969)

$$S = 2\pi \int_{\frac{\theta_s}{2}}^{\pi} \frac{I_{\theta_s}}{I_{\infty}} \sin \theta_s \, d\theta_s$$

(16)

where $\theta_s$ is the angle of light scattering with respect to the positive x axis; $I_{\theta_s}$ is the flux of radiation scattered at an angle of $\theta_s$; and $I_{\infty}$ is the total scattered radiation flux.

Equation 15 can be solved explicitly for $K/S$ to obtain the Kubelka-Munk function

$$\frac{K}{S} = \frac{(1-R_{\infty})^2}{2R_{\infty}} = F(R_{\infty})$$

(17)

It is of great import that $R_{\infty}$ is a function only of $K/S$. In other words the reflectivity depends exclusively on the ratio of the absorption and scattering coefficients, and not on their absolute values.

Kubelka-Munk Solution for a Finite Layer of Particles Overlying an Infinite Layer

To solve explicitly for the reflectance, $R$, of a finite layer, Equation (15) can be rearranged to solve for $a$, such that

$$a = \frac{1}{2} \left( \frac{1}{R_{\infty}} + R_{\infty} \right)$$

(18)
and introduce $b$, such that
\[ \sqrt{a^2 - 1} = b \]  
(19)

so Equation (18) becomes
\[ \sqrt{a^2 - 1} = b = \frac{1}{2} \left( \frac{1}{R_z} - R_x \right) \]  
(20)

From Equations (15) and (20)
\[ R_x = a - b = \frac{1}{a + b} \]  
(21)

Inserting Equation (18) and (20) in Equation (13) we obtain for a layer of finite thickness $X$
\[ \ln \left( \frac{R - \frac{1}{R_x}}{R_z - \frac{1}{R_x}} \right) = S X \left( \frac{1}{R_x} - R_x \right) \]  
(22)

which can be solved for $R$, the reflectance of a finite layer,
\[ R = \frac{\left( \frac{1}{R_x} \right) \left( R_z - R_x \right) - R_x \left( R_z - \frac{1}{R_x} \right) \cdot \exp \left[ S X \left( \frac{1}{R_x} - R_x \right) \right]}{\left( R_z - R_x \right) - \left( R_z - \frac{1}{R_x} \right) \cdot \exp \left[ S X \left( \frac{1}{R_x} - R_x \right) \right]} \]  
(23)

Hence, the reflectance of a finite layer, of thickness $X$, is a function of the reflectance of the backing, $R_z$, the reflectance of an analogous but infinitely thick layer, $R_x$, and the product $S X$, which is called the "scattering power" of the sample. The absorption coefficient, $K$,
does not appear in Equation 23 but is implicitly contained in the value of $R_e$, which is a function of $K/S$ (see Equation 17).  

Assumptions and Limitations of Kubelka-Munk Solution  

There are a number of assumptions and approximations inherent in the Kubelka-Munk approach, which simplifies a very complex three dimensional problem into one dimension. It is assumed that no reflection loss occurs at the surface because of a change in refractive index. Hence, the host medium (matrix or vehicle) containing the scattering particles must be the same as that from which the radiation impinges on the surface of the layer (Kortüm, 1969). In practice only particles imbedded in air (refractive index of 1.0) meet this criteria. Air (above and within the media) is assumed not to significantly alter the light radiation in any way (no refraction and no absorbance, i.e., colorless). Scattering coefficients are caused only by particulate-air interfaces. Hence, the equations are not valid in the presence of moisture. Suspensions in liquids require additional terms to correct for the surface reflection loss at the air-liquid interface.  

It is assumed that the scattering and absorption coefficients, $S$ and $K$, are the same value throughout the layer. All particles are
considered to be uniformly distributed and oriented in a random way in order to produce perfect diffusion of light within the layer. The medium is assumed to produce ideal diffuse (isotropic) reflection. It is assumed that the incident light flux is perfectly diffuse. All layers, including the top-most elementary layer, are considered to receive diffuse fluxes from above and below. This is an important assumption for calculating the actual pathlength traversed by the diffused light. In reality, we normally illuminate the sample with a collimated beam of parallel light. If a parallel beam at 60° to the surface normal is used, the actual pathlength to geometrical pathlength is 2 as in the case of diffused illumination (i.e., \( \cos(60°) = 0.5 \)). Identical results are obtained with diffuse and parallel incidence for powders, hence the diffusion of light within the sample appears to be complete (Wendlandt and Hecht, 1966). Diffuse and parallel incident light systems become identical when the material is perfectly dull and when the light is perfectly diffused or if it is parallel and hits the specimen under an angle of 60° from normal (Kubelka, 1948). Another assumption is that the medium does not emit radiation or fluoresce.
Experimental Methodology

Water sediments are quantified physically based on their mass using the method of Strickland and Parsons (1968). Water samples are filtered on pre-combusted and tared glass fiber filters (Whatman, GF/F, 0.7 micron). Sediments are dried for one hour at 60°C, instead of the recommended 75°C, to minimize the breakdown of proteins. Instead of throwing the filter paper away at the end of the analysis, the dried sediments are scanned with an inexpensive, hand-held spectrophotometer to measure their reflectance. The spectrophotometer (Colortron II from Light Source, Inc., Larkspur, California) is a 32-band color sensor traditionally used in the graphics arts field. The instrument uses a diffraction grating analyzer with twin tungsten lamps at 45° on both sides of the scanned area for illumination geometry. The system is entirely enclosed and unaffected by external lighting. The instrument measures reflectance over an area of 3 mm² every 10 nm from 390 to 700 nm (visible range). The spectrophotometer is placed directly on top of the filter with sediments and a complete scan requires about 10 seconds. The instrument is calibrated daily by scanning a black box (0 percent reflectance).
and a white standard reflector unique to the instrument. Hence, all values of reflectance are relative to this standard, which is assumed to be a perfect scattering media ($R = 1.0$). Calibration was checked with gray and white standards.

The mass of sediment on the filter paper was varied and measured for each sediment sample by filtering a range of water sample volumes. This provided a range of sediment masses and thicknesses on the filter paper. To insure a homogeneous, intimate mixture of particles, reflectance readings were only measured for sediment loadings which were sufficient to entirely cover the filter paper with at least one monolayer of particles. The reflectance of the series of sediment loadings was measured for each sediment type by scanning the filtered sediments in 4 different locations on the filter. Three different sediments representing various extreme scattering and absorption properties were measured to identify the limitations of the technique. The Kubelka-Munk model is tested to see how well it fits the experimental data.
Analytical Methodology: Application of the Kubelka-Munk Equations to Suspended Solids on a Filter Paper

We now link the approximate radiative transfer equations of Schuster and Kubelka-Munk to the total suspended solids analysis. We consider Equation 23 with respect to a mass of sediments on a filter paper. The filter paper simply becomes the backing paper (x=0). In the case of a white filter paper, $R_g \to 1$, and is measurable (we simply scan the blank filter paper). We can filter various volumes of water samples containing suspended solids to produce various amounts (thicknesses) of sediments on the filter paper. Moreover, we know the exact mass of the particulates on the paper (which we measure) and the depth represented by the mass (volume of water sample divided by area of filter paper). Hence, we can easily link optical properties to mass of solids and depth of water. We can increase the volume of the water sample passed through the filter paper until the sediment layer becomes optically thick. In many cases, however, it will not be possible to obtain an optically, infinitely thick layer of sediment on the filter paper. In either case we measure values of reflectance, $R$, for various mass loading rates on the filter paper. The only variable that is not
exactly analogous to traditional Kubelka-Munk applications (in the graphic arts) is \( X \), the sample thickness. Fortunately, \( X \) can be related to other easily measureable quantities, specifically the mass of solids or the depth of water sample filtered. The actual thickness (on the order of mm) of the layer of particulates is not easily measurable, nor meaningful for water quality applications. In our case we may use the depth of water sample filtered given by

\[
X \rightarrow X_d \quad \text{where} \quad X_d = d = \frac{V}{A_f} \quad [\text{length}]
\]

where \( V \) is the volume of water sample filtered to attain a certain thickness, \( X \), on the filter paper; and \( A_f \) is the area of the filter paper containing solids. \( X_d \) has units of (m) and the scattering coefficient \( S \), based on depth becomes, \( S_d \), with units of (m\(^{-1}\)).

Another option is to assume that the thickness, \( X \), is directly proportional to the mass of sediment on the filter paper. Hence, we define \( X \) in terms of mass of solids per unit area of filter such that

\[
X \rightarrow X_m \quad \text{where} \quad X_m = \frac{m}{A_f} \quad \left[ \frac{\text{mass}}{(\text{length})^2} \right]
\]

where \( X_m \) is the mass loading of solids to obtain a certain thickness, \( X \), on the filter paper. \( X_m \) has units of (g/m\(^2\)) and the specific
scattering coefficient $S$, based on mass becomes, $S_m$, with units of $(m^2/g)$.

Also, $X_m$ is linearly proportional to $X_d$:

$$X_m = TSS \cdot X_d$$

and

$$S_m = TSS \cdot S_d$$

so it is easy to convert calculated coefficients between units of mass and depth.

**Nonlinear Least Squares Regression of Equation 23**

Making the direct substitution of $X_m$ for $X$ in Equation 23, our analytical problem is to find the values of $S_m$ and $R_x$ which minimize the sum of the square of the errors for a given set of measured $X_m$ and $R$ values. Our error is defined as the difference between the observed reflectance $R$, and the value of $R$ predicted by Equation 23. Because we always use the same type of filter, we assume, $R_y$, is a measurable constant. The best values of the model parameters ($S_m$ and $R_x$) for a given set of $X_m$, $R_y$, and $R_{\text{observed}}$ data are numerically calculated by using the Levenburg-Marquardt procedure to minimize the sum of the square errors. The Levenburg-Marquardt procedure utilizes matrix inversion with
each iteration, which is done by using the Gauss-Jordan method. Given the best values of \( R_s \) and \( S_m \), values of \( K (K_m) \) can be calculated with the Kubelka-Munk Equation (Equation 17) for an infinitely thick layer.

Results

Three water sediment types representing extreme scattering and absorption properties were analyzed by the proposed methodology in Table 5.1. A pure algal culture of *Chlamydomonas reinhardtii* was used to represent highly absorbing sediments. Suspended solids from the Mississippi River during flood stage in Baton Rouge, Louisiana (March 23, 1997) represented scattering sediments with little absorption. A culture of bacteria from an aerobic aeration pond of a chemical plant's wastewater treatment plant was analyzed to represent an organic sediment with small particle size and little absorption.

The method outlined in Table 5.1 was applied to the three sediment types. Figure 5.3 shows the relationship between \( R \) and \( X_m \) as a function of wavelength for the algae. The bottom line represents \( R_s \) predicted by the NLS model. Figure 5.4 shows the difference between observed and theoretical reflectance for the
Table 5.1. Summary of Experimental and Analytical Methodology

**Experimental Methodology**

1. Scan Blank Filter (Measure $R_g$)
2. Run TSS Analysis (Measure $X_m$)
3. Scan TSS on Filter Paper (Measure $R$)

Repeat Steps 1-3 for various $X_m$ to obtain

$$R_{obs} = f (X_m)$$

**Analytical Methodology**

Apply Nonlinear Least Squares to RTT Equation for a finite layer to obtain values of $R_x$ and $S_m$

Given the best values of $R_x$ and $S_m$, use the RTT Equation for an infinite layer to calculate $K_m$
Figure 5.3. Reflectance and wavelength of algae for various masses on filter paper (area of filter = 0.00105 sq. m).
Figure 5.4. Kubelka-Munk model fitted to reflectance of algae at 440 nm.
algae at a wavelength of 440 nm. Figure 5.5 shows values of \( R_* \) predicted by the NLS model for all three sediments. The values of \( R_* \) are converted to 1931 CIE XYZ (Commission Internationale de l'Éclairage) tristimulus values (Table 5.2) for the various sediments. The values of the scattering coefficients, \( S_m \), are shown in Figure 5.6 and the absorption coefficients, \( K_m \), in Figure 5.7.

Discussion

The coefficients determined with the Kubelka-Munk equation (Equation 23) must be carefully interpreted based on the limitations, approximations and assumptions that go into the equation. We wish to determine if application of the Kubelka-Munk equations to Total Suspended Solids provides a useful quantitative tool to compare the optical differences between TSS filtered from different water samples. To do this, we will discuss our results in light of the definitions of the Kubelka-Munk coefficients, \( K \) and \( S \).

Hapke (1993) has pointed out that the parameters \( K \) and \( S \) of the Kubelka-Munk equations are often misinterpreted. For example, light which is forward scattered is interpreted as
Figure 5.5. Predicted reflectance of an infinite layer for the three sediment types.
Table 5.2. 1931 CIE XYZ tristimulus values for the three types of suspended solids.

<table>
<thead>
<tr>
<th>Sediment</th>
<th>X</th>
<th>Y</th>
<th>Z</th>
</tr>
</thead>
<tbody>
<tr>
<td>Algae, <em>Chlamydomonas reinhardtii</em></td>
<td>18.4</td>
<td>22.2</td>
<td>7.6</td>
</tr>
<tr>
<td>Mississippi River Sediments, Baton Rouge, Louisiana</td>
<td>32.2</td>
<td>32.9</td>
<td>21.0</td>
</tr>
<tr>
<td>Wastewater Bacteria, Chemical Plant</td>
<td>39.3</td>
<td>39.0</td>
<td>25.0</td>
</tr>
</tbody>
</table>
Figure 5.6. Specific scattering coefficients for the three sediment types.
Figure 5.7. Specific absorption coefficient for the three sediment types.
unscattered by Kubelka and Munk. This arbitrary definition implies that $S$ should be replaced by $S/2$ (reduced by a factor of 2) in practice. Moreover, because of its arbitrary definition, the value of $S$ is not directly related to the refractive index and size of the particles.

Despite these constraints on the scattering coefficient, the Kubelka-Munk equation does provide a physically meaningful value for the absorption coefficient, $K$. The value of this parameter represents the volume absorption coefficient and not the average internal absorption coefficient of the particles. Kortum has pointed out that relative to transmission measurements, the absorption spectra from reflectance measurements are flattened (lower peaks and higher valleys). Hapke (1993) interprets the Kubelka-Munk $K$ to be equal to

$$K = \sum_i N_i \sigma_i Q_{\lambda i}$$  \hspace{1cm} (28)

in which $j$ denotes different types of particles making up the layer, $N$ is the number of particles per unit volume, $\sigma$ is the geometrical cross sectional area of the particle, and $Q_{\lambda}$ is the absorption efficiency of a single particle given by
where \( \sigma_A \) is the absorption cross section of the particle. \( \sigma_A \) represents the ratio of absorbed radiation (by a particle) to incident irradiance. Hence, the value of the absorption coefficient, \( K \), represents the aggregate effect of the number of particles per unit volume and their respective absorbing properties.

In a similar way, the scattering coefficient may be interpreted as being a combined parameter integrated over the number, type, and scattering properties of all particles making up the layer. Hence, \( S \), is given by (Hapke, 1993)

\[
S = \sum_j N_j \frac{\sigma_j Q_{s_j}}{2}
\]

in which \( Q_{s_j} \) is the scattering efficiency analogous to the absorption efficiency.

In the case of interest, in which the TSS particles are large relative to the wavelengths, we also have the relation (Hapke, 1993)

\[
Q_{s_j} + Q_{a_j} = Q_B = 1
\]

where \( Q_B \) is the extinction efficiency. Equation 31 shows the link between absorption and scattering and explains why values of \( S \)
depend on the absorption coefficient, $K$. Combining Equations 30 and 31 enables us to rewrite the scattering coefficient as

$$S = \frac{\sum_j N_j \sigma_j (1 - Q_{\lambda_j})}{2}$$

which may be written in terms of $K$, by incorporating the definition of $K$ from Equation 28

$$S = \frac{\sum_j N_j \sigma_j - K}{2}$$

It is obvious from Equation 33 that the scattering coefficient of the Kubelka-Munk analysis is linearly dependent on the absorption coefficient, which in turn, depends on the number, type, and absorption properties of the particles making up the layer. The reason $S$ varies with wavelength is because the value of $K$ is generally wavelength dependent.

The NLS model of Equation 23 permits the prediction of the reflectance of an infinite layer (by using reflectances of sequential finite layers) of suspended solids on a filter paper. The shape of the backscattering curves (Figure 5.6), shows increased scattering with increasing wavelength for the bacteria and river. This is due to the fact (see Equation 33) that the absorption coefficient is decreasing with increasing wavelength. Despite being flattened, the
absorption curve for the algae in Figure 5.7 matches well with published shapes of algal cultures (Perry, 1994). As expected, the smaller sized bacteria show significantly greater scattering and absorption on a per mass basis than the other two sediment types. Research by others has shown that the value of S from Kubelka-Munk analysis is of the order of the reciprocal of the particle size (Hapke, 1993). The absorption curve (Figure 5.7) of the river sediments also agrees with the typical curves of seston absorption (Bowers et al., 1996).

Conclusions

The proposed methodology, based on linking the approximate radiative transfer theory of Kubelka and Munk with the traditional total suspended solids analysis, enables rigorous and quantitative comparison of spectrally different sediments. Although the calculated coefficients represent multiple scattering for dried sediments, they contribute to the understanding of remote sensing images of natural waters and bio-optical models which consider packaging effects. The methodology has laboratory analytical applications for the estimation of pigments. The low-cost, rapid technique also provides a quantitative means for assigning the
attribute of color to the particulate population in natural waters, which contributes to the tracing of sediment sources and is readily understandable to the general public. Application of the Kubelka-Munk equation to total suspended solids provides a useful tool for optically quantifying their absorption properties. Careful interpretation of the Kubelka-Munk scattering coefficient also provides insight into scattering by TSS particles.
In this Chapter, a method for measuring the absorbing and scattering properties of a layer of dried Total Suspended Solids (TSS) on a filter paper is presented. The method is based on linking reflectance spectroscopy and radiative transfer theory to the typical TSS analysis, in which the mass of sediments on the filter paper is measured. This Chapter begins by reviewing the Hapke bidirectional reflectance model in detail, the model is then modified to incorporate the mass measurements of the TSS analysis. This modification enables the Hapke model to be applied to Reflectance and TSS data to determine the fundamental scattering and absorption properties of the TSS. Optical parameters of the TSS are obtained by using a nonlinear least squares, curve fitting technique which matches the theoretical equations to the experimental data. The required laboratory measurements are simple, inexpensive, convenient, and quickly obtained. In fact, the proposed experimental technique adds approximately 30 seconds
to the typical TSS analysis (which normally takes about two hours).

The experimental and theoretical methodologies are demonstrated on three typical water sediment types (algae, bacteria, and river sediments) which cover a wide range of absorbing and scattering properties.

Fundamental Definitions of the Hapke Bidirectional Reflectance Model

The Hapke (1981, 1993) reflectance model is based on the way a layer of particles reflects light which is incident upon it. Reflectance refers to the fraction of incident light which is scattered or reflected by a surface towards a viewer. The strength of Hapke's model over previous models based on reflectance spectroscopy, such as the Kubelka-Munk model, is the rigorous definition of the fundamental optical properties of the particles and the careful treatment of the directional nature of the reflectance. Like the Kubelka-Munk model, Hapke's model is based on the approximate two-stream radiative transfer equation for closely packed particulate media. However, the parameters of the Kubelka-Munk model are arbitrarily defined and assume a diffusive distribution of the incident, reflected, and emitted
radiation. The Hapke model, on the other hand, is based on physically meaningful parameters, enables linking of fundamental properties of the particles with the observed, directional reflectance. Conversely, the fundamental properties of the particles can be found from measured values of reflectance. We will now review several fundamental properties and definitions which are the basis of the Hapke model.

**Irradiance and Radiance Defined**

Light may propagate in collimated (parallel) or uncollimated (multi-directional) rays. Irradiance refers to the power of a collimated beam per unit area and radiance is the power of an uncollimated beam per unit area per unit solid angle (Figure 6.1). The sun’s light incident on the earth can be considered as collimated and propagating in one direction. Once sunlight strikes the earth’s rough surface, however, it becomes uncollimated as it reflected in numerous directions. A similar situation occurs when one measures reflectance of a layer of particles in the laboratory. The light source is considered collimated (irradiance) and the scattered light is considered uncollimated (radiance). In the
Figure 6.1. Irradiance, $J$, and radiance, $I$. Irradiance = power/unit area. Radiance = power/unit area/solid angle (Hapke, 1993).

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extreme, scattered radiation can be reflected equally in all directions. This is what occurs when sunlight interacts with nearly perfect isotropic scatterers, such as a cloud, and this is termed diffusive reflectance.

**Fundamental Absorption and Scattering Properties of Particles**

Hapke (1993) presented optical parameters for a particle subjected to light radiation and demonstrated how they relate to the radiance emerging from a layer of closely packed particles. We consider a particle of cross-sectional area, $a$. If the particle is a sphere of diameter, $D$, then

$$a = \frac{\pi}{4} D^2$$

(1)

If the particle is irregular in shape, we may still use the concept of a cross-sectional area as long as we consider the particle at all possible orientations (Hapke, 1993). In this case, $a$ is the average projected cross-sectional area of all possible orientations. This particle (Figure 6.2) will scatter and absorb a fraction of the total power of the incident irradiance, $J$. The irradiance is scattered by an angle of $\theta$ from its original direction. The phase angle, $g$, is the...
Figure 6.2. Scattering by a particle (Hapke, 1993).
complementary angle of \( \theta \). Hapke (1993) defines the extinction cross section of the particle as

\[
\sigma_E = \frac{P_E}{J} \tag{2}
\]

where \( P_E \) is the total amount of the incident power affected by the particle. A portion of the incident power is scattered into all directions, and the remainder is absorbed by the particle. The scattering cross section is

\[
\sigma_s = \frac{P_s}{J} \tag{3}
\]

where \( P_s \) is the power scattered by the particle. The absorption cross section is

\[
\sigma_A = \frac{P_A}{J} \tag{4}
\]

where \( P_A \) is the power absorbed by the particle.

We note that cross sections have units of area. Because the total power affected by the particle is the sum of the scattered and absorbed power, then
Efficiencies are defined by Hapke (1981; 1993) as the ratio of the cross sections to the geometrical cross-sectional area of the particle, such that the extinction efficiency, \( Q_E \), is

\[
Q_E = \frac{\sigma_E}{\sigma}
\]

the scattering efficiency, \( Q_S \), is

\[
Q_S = \frac{\sigma_S}{\sigma}
\]

the absorption efficiency, \( Q_A \), is

\[
Q_A = \frac{\sigma_A}{\sigma}
\]

and

\[
Q_E = Q_S + Q_A
\]

Hapke defines the ratio of the total amount of power scattered to the total power affected by the particle as the particle single-scattering albedo, \( \omega \).
\[ w = \frac{P_S}{P_E} = \frac{\sigma_S}{\sigma_E} = \frac{Q_S}{Q_E} \]  

(11)

\( w \) is the fundamental quantity in reflectance spectroscopy of particles (Hapke, 1993). A parameter related to \( w \), which often appears in reflectance equations, called the albedo factor, \( \gamma \), is defined as

\[ \gamma = \sqrt{1 - w} \]  

(12)

The ratio of the absorption and scattering efficiencies (Hapke, 1993) is defined as \( W \), the effective single-particle absorption-thickness (espar) function given by

\[ W = \frac{Q_A}{Q_s} = \frac{1 - w}{w} \]  

(13)

**Volume Averaged Coefficients**

Hapke (1993) has shown that the optical parameters of individual particles may be extended to the medium of closely packed particles. This is accomplished by multiplying the number of particles per unit volume, \( N \), by their cross-sectional area and particle efficiency of interest. For example, the extinction coefficient of a medium of uniform particles is

\[ E = N \sigma Q_e \]  

(14)
Similarly, the scattering and absorption coefficients, $S$ and $K$, of a medium of one type of particle are given by

$$S = N \sigma Q_s \quad (15)$$

$$K = N \sigma Q_a \quad (16)$$

If the medium is made up of an intimate mixture of more than one type of particle, then the volume averaged coefficients become

$$E = \sum_j N_j \sigma \phi_j Q_{\phi j} \quad (17)$$

$$S = \sum_j N_j \sigma \phi_j Q_{\phi j} \quad (18)$$

$$K = \sum_j N_j \sigma \phi_j Q_{\phi j} \quad (19)$$

where $j$ refers to the $j$-th type of particle. We note that $E$, $S$, and $K$ have units of $1$/length and that

$$E = S + K \quad (20)$$

The volume single-scattering albedo is given by (Hapke, 1993)

$$w_v = S/E \quad (21)$$

If only one type of particle makes up a medium, then the volume single-scattering albedo reduces to the single-scattering albedo ($w_v = w$).

In this Dissertation, a methodology for obtaining the values of the $w$ and $W$ functions will be derived for Total Suspended Solids.
on a filter paper. These functions will be expressed in terms of the wavelength for various TSS.

The Size Parameter and its Effect on Scattering

How light interacts with a particle depends primarily on the size of the particle relative to the wavelength of the incident radiation. It is the scattering, or change in direction of radiation, which is very sensitive to the size of particles. Three scattering regimes are generally considered: 1) when the particle is much smaller than the wavelength, 2) when the particle and wavelength are similar in size, and 3) when the particle is much larger than the wavelength. In order to quantify the relationship between size of particles and wavelength, the following ratio, known as the size parameter, is often used

$$X_\lambda = \pi \frac{D}{\lambda} \tag{22}$$

Vastly different scattering regimes are produced depending on the value of $X_\lambda$ in comparison to unity. For example, when $X_\lambda$ is much smaller than 1, the scattered radiance is proportional to $1/\lambda^4$ for a nonabsorbing particle. These small particles are known as Rayleigh scatterers. In the case of $X_\lambda$ on the order of 1, the scattering efficiency tends to oscillate. The case of $X_\lambda >> 1$ is known as the
geometric optics region, in which the plane surface of the particle may be considered infinite relative to a beam of light. In this region, the particle refracts and reflects light depending on whether or not it is isolated from neighboring particles. If a large particle is isolated from its neighbors, then diffraction occurs in addition to refraction and reflection of light incident on the particle (Figure 6.3). Due to diffraction, an isolated particle affects an area of a light wave front of approximately twice its cross-sectional area. Hence, for a large, isolated particle, $Q_k = 2$ (Hapke, 1993). Diffraction causes scattering to be predominantly forward in direction for large, isolated particles.

The geometric optics region is of interest in this Dissertation because most suspended sediments are relatively large compared to the visible wavelengths. In the case of bacteria, very fine clay particles, and viruses this assumption may no longer be valid. We shall now consider the effect of particle spacing on scattering.

**Effect of Particle Spacing on Diffraction and Extinction**

We will now consider the spacing between particles, and its effect on the above parameters. Diffraction refers to the bending of light around objects. It is this wavelike behavior in the vicinity of
Figure 6.3. Scattering by an isolated particle (Hapke, 1993).
an isolated particle which causes the beams of light near an object to scatter or alter direction. This is the phenomenon which causes the pronounced forward scattering of isolated particles. Diffraction is "associated with scattering by the particle because constructive interference of Huygens wavelets from light that passes through a complete annulus around the particle generates a wave that appears to radiate from the particle into a narrow cone of approximate angular width $\pi/X_0$ about the forward direction" (Hapke, 1993). Total suspended solids on a filter paper, on the other hand, are packed closely together, such that they are touching. Diffraction occurs in the open spaces around particles. When these spaces are filled with neighboring particles (as is the case for soils and TSS on a filter paper), the angular deviation due to diffraction becomes negligible and the extinction efficiency approaches unity ($Q_e = 1$). In other words, the light traveling in the tiny spaces between particles does not change direction until it encounters a particle. The fact that $Q_e=1$ implies that any light incident on a particle will be altered, either by scattering or absorption. Hence, the interactions of light and the particle will depend only on specular (mirror-like) reflection from the surface.
and refraction, absorption, and internal reflections within the particle of the transmitted radiation (all of these processes are, of course, limited to within the geometric cross-sectional area, \( \sigma \)). This implies that for large and closely packed particles we have

\[
Q_E = 1 = Q_s + Q_a
\]

Hence, the scattering and absorption efficiencies are linked (not independent), if we can estimate or measure one, then the other is also known. Another important advantage of the absence of diffraction is that the particle single-scattering albedo, \( w \), (the primary reflectance parameter), becomes equivalent to the scattering efficiency of a single particle, or

\[
w = Q_s
\]

Geometry of Reflectance Measurements

Unlike the Kubelka-Munk equations, which assume diffusive reflectance regimes, the Hapke equations consider the directional components of incident and scattered light. Figure 6.4 shows the geometry of directional reflectance measurements. A given reflectance measurement is associated with the geometry of the source with respect to the detector. The three angles used to define the geometry in Figure 6.4 are the angle of incidence, \( i \), the angle of
Figure 6.4. Geometry of bidirectional reflectance (Hapke, 1993).
emergence, $e$, and the phase angle, $g$. The angles $i$ and $e$ are measured with respect to the normal vector. The angle between the detector and the source as viewed from the surface is the phase angle, $g$. The angle $g$ is the complement of the scattering angle, $\theta$ ($g = \pi - \theta$). Because the cosines of the angles of incidence and emergence appear in many reflectance equations, they are often defined conveniently in terms of single Greek letters as

$$\mu_0 = \cos i$$  \hspace{1cm} (25)

$$\mu = \cos e$$  \hspace{1cm} (26)

The Bidirectional Reflectance

When discussing reflectance values, two adjectives are generally used (Nicodemus, 1977; Nicodemus et al., 1977; Hapke, 1993) to describe the measured reflectance. The first adjective refers to the degree of collimation of the light source, which may range from collimated (directional) to hemispherical. Similarly, the second adjective refers to the degree of collimation of the detector, which may also range from directional to hemispherical. If the source and detector have the same degree of collimation, the prefix, $bl$-, is used for convenience. Hence, if the reflectance of a medium subjected to a collimated light source is measured with a
collimated detector, the reflectance is called bidirectional reflectance. Since most commercial reflectance spectrophotometers utilize a collimated source and detector, the measured reflectance is considered as a bidirectional reflectance.

The bidirectional reflectance, \( r(i, e, g) \), is defined as the ratio of the scattered radiance, \( I_D \), at the detector to the incident irradiance, \( J \) (Hapke, 1993)

\[
r(i, e, g) = \frac{I_D}{J}
\]

We note that the bidirectional reflectance has units of radians\(^{-1}\).

The bidirectional-reflectance distribution function as defined by Hapke (1993) is the "ratio of the radiance scattered by a surface into a given direction (which equals \( J \cdot r(i, e, g) \)) to the collimated power incident on a unit area of the surface (which equals \( J \cdot \mu_0 \))." \( r(i, e, g) \) is the bidirectional reflectance of the surface.

Hapke (1981) derived an approximate, analytical solution for the bidirectional reflectance of a semi-infinite particulate medium. Hapke's theory utilizes the two-stream radiative transfer equation for irregular particles that are close together. The solution for isotropic scatterers is
Bidirectional Reflectance and Relative Reflectance

Many spectrophotometers do not measure bidirectional reflectance directly. Instead, they quantify reflectance relative to a standard, which is assumed to be made up of an infinitely thick layer of nonabsorbing, isotropic scatterers. Both the standard and the sample are illuminated and viewed under the same geometry. Such a standard would have a $w=1$ ($\gamma=0$) with an associated bidirectional reflectance of

$$r_{w=1}(i,e,g) = \frac{1}{4\pi} \frac{\mu_0}{\mu_0 + \mu} \frac{1 + 2\mu_0}{1 + 2\gamma \mu_0} \frac{1}{1 + 2\gamma \mu}$$

(29)

The relative reflectance, $\Gamma(i,e,g)$ as measured by a typical spectrophotometer, is then the ratio of the bidirectional reflectance of the sample to the bidirectional reflectance of white standard

$$\Gamma(i,e,g) = \frac{r_{\text{sample}}(i,e,g)}{r_{w=1}(i,e,g)}$$

(30)

For an isotropic sample, the relative reflectance is

$$\Gamma(i,e,g) = \frac{4\pi(\mu_0 + \mu)}{\mu_0(1 + 2\mu)(1 + 2\mu)} r_{\text{sample}}(i,e,g)$$

(31)

Hence, if the relative reflectance of a sample is measured by a spectrophotometer (with its associated geometry of $\mu_0$ and $\mu$), and

$$r(i,e,g) = \frac{w}{4\pi} \frac{\mu_0}{\mu_0 + \mu} \frac{1 + 2\mu_0}{1 + 2\gamma \mu_0} \frac{1 + 2\mu}{1 + 2\gamma \mu}$$

(28)
we wish to calculate the bidirectional reflectance of the sample, we may solve Equation 31 for $r_{\text{sample}}(i, e, g)$

$$r_{\text{sample}}(i, e, g) = \frac{\mu_0(1 + 2\mu_0)(1 + 2\mu)}{4\pi(\mu_0 + \mu)} \Gamma(i, e, g)$$ (32)

For brevity, we will generally drop the 'sample' subscript.

Bidirectional Reflectance of an Infinite Layer of Particles

The bidirectional reflectance of an optically thick (opaque) layer of isotropic scatterers is easily measured with a spectrophotometer. Hence, the determination of the scattering and absorption properties of a thick layer of particles is a straightforward practice, requiring only one reflectance measurement for any given geometry (angle of incidence, $\mu_0$, and angle of observation, $\mu$). Once the bidirectional reflectance, $r(i, e, g)$ is known, the only unknown in the equation is $w$. We recall that $w$ and $\gamma$ are related by the simple definition:

$$\gamma = \sqrt{1-w}$$ (33)

Given, the geometry and observed reflectance, we may calculate the value of $w$, the particle single-scattering albedo, which is defined as the ratio of the scattering and extinction efficiencies, $Q_s/Q_e$, of the particles. From the scattering efficiency, we may
calculate the ESPAT Function, \( W \), which is the ratio of the absorption efficiency to scattering efficiency.

\[
W = \frac{Q_\perp}{Q_s} = \frac{1 - w}{w}
\]  \hspace{1cm} (34)

For anisotropic scatterers, the bidirectional reflectance of an infinite layer is approximated by (Hapke, 1993)

\[
r(i, e, g) = \frac{w}{4\pi} \frac{\mu_0}{\mu_0 + \mu} \left[ p(g) + \frac{1 + 2\mu_0}{1 + 2\gamma_0} \frac{1 + 2\mu}{1 + 2\gamma} - 1 \right]
\]  \hspace{1cm} (35)

where \( p(g) \) is the particle phase function, which describes the angular distribution of scattering.

**Bidirectional Reflectance of a Finite Layer of Particles**

In this Chapter, the Hapke Bidirectional Reflectance Model for a finite layer of particles overlying an infinite layer of particles (Figure 6.5) is presented (Hapke, 1993), followed by it's application to quantifying the optical properties of total suspended solids on a filter paper. Although the bidirectional reflectance of an infinite layer is easily measured and interpreted, we must resort to the more complicated equations for a finite layer. The equations are complicated by the fact that they must take the layer thickness into account, as well as the optical contribution of the underlying layer on which the finite layer rests. Except for highly absorbing
Figure 6.5. Geometry of two-layer bidirectional reflectance (Hapke, 1993).
particles, an optically thick (opaque) layer of particles is not achievable on a filter paper in the laboratory. Practical limitations to achieving an infinite layer include filter clogging, extremely long filtration times, nonuniformity, and inaccurate mass measurements and incomplete drying. The bidirectional reflectance, \( r(i, e, g) \), is the ratio of the radiation scattered to a detector, \( I_D \), to the collimated irradiance, \( J \), incident on a medium. Bidirectional reflectance is composed of singly and multiply scattered components

\[
 r(i, e, g) = \frac{I_D}{J} = r_s(i, e, g) + r_m(i, e, g) \quad (36)
\]

The values of \( i \), \( e \), and \( g \) are in radians, and refer to the angles of incidence, emittance, and phase, respectively, for the geometry of the optical measuring system as depicted in Figure 6.5. To simplify the notation, we recall that \( \cos i \) is \( \mu_0 \), and the \( \cos e \) is \( \mu \).

The singly scattered component is given by (Hapke, 1993)

\[
 r_s(i, e, g) = \frac{\mu_0}{\mu_0 + \mu} \left[ \frac{w^L_pL(g)}{4\pi} \left[ 1 - e^{-\frac{1}{\mu_0}} \right] + \frac{w^L_pL(g)}{4\pi} \left[ e^{-\frac{1}{\mu_0}} \right] \right] \{1 + B(g)\} \quad (37)
\]

where \( p_u(g) \) and \( p_L(g) \) are the phase functions for the upper and lower layers, respectively. The phase functions define the angular pattern into which the radiation is scattered. If isotropic scattering
is assumed, then the scattering distribution is independent of phase angle and the phase functions, which are normalized, become unity. Forward scattering particles, which scatter most of the incident light into the forward hemisphere are described by

\[ p(g) = 1 - \cos g \]

Similarly, backscattering particles are represented by

\[ p(g) = 1 + \cos g \]

At small phase angles, the opposition effect (also known as *hot spot*) becomes important in the singly scattered component. This effect, which causes a surge in brightness around zero phase angle (when the viewing and incident directions are very close) is attributed to the fact that the openings between particles act as tunnels which are illuminated only at small phase angles. These tunnels can be thought of as cylinders with diameters representing the average distance between particles. At larger phase angles, the tunnels are hidden from view. The opposition effect is quantified by including a term, \( B(g) \), to account for increased reflectance of the openings between particles when viewed at small phase angles.

The multiply scattered component is given by (Hapke, 1993)
where the constants $A_U$, $A_L$, $B_U$, $C_U$, and $C_L$ are defined by (Hapke, 1993)

\[ A_U = \frac{1}{1 + \gamma_U} B_U = \left[ \frac{1 + \frac{1}{2\mu_0}}{1 + \gamma_U} \right] C_U \]  (39)

\[ A_L = -\frac{2\gamma_L e^{2\gamma_L r_0} B_U - (C_L - C_U) \gamma_U - \frac{1}{2\mu_0} e^{\frac{-r_0}{\mu_0}}}{\gamma_L - \gamma_U} \]  (40)

\[ B_L = \frac{\left( \frac{C_U}{1 + \gamma_U} \right) \left( 1 + \frac{1}{2\mu_0} \right) (\gamma_L - \gamma_U) e^{-2\gamma_L r_0} + (C_L - C_U) \left( \gamma_L - \frac{1}{2\mu_0} \right) e^{\frac{-r_0}{\mu_0}}}{(\gamma_L - \gamma_U) e^{2\gamma_L r_0} - \left( \frac{1 - \gamma_U}{1 + \gamma_U} \right) (\gamma_L - \gamma_U) e^{-2\gamma_L r_0}} \]  (41)

\[ C_U = \frac{1 - \gamma_U^2}{1 - 4\mu_0^2 - \gamma_U^2} \]  (42)

\[ C_L = \frac{1 - \gamma_L^2}{1 - 4\mu_0^2 - \gamma_L^2} \]  (43)
Equations 36 through 43 include multiple scattering within and between the two layers. We note that the multiply scattered component does not include a phase function term, \( p(g) \). This because multiple scattering produces an isotropic scattering regime (Hapke, 1993). The opposition effect, which is the result of singly scattered light, is also insignificant in the multiply scattered component.

Modification of the Hapke Bidirectional Reflectance Model to Total Suspended Solids on a Filter Paper

We now apply the Hapke reflectance model to reflectance data of total suspended solids on a filter paper. We write the Hapke equations in terms of mass loading rate on the filter and curve fit the reflectance data to find the best value of \( \gamma \), the albedo factor. Other, more fundamental optical parameters may then be calculated from the albedo factor. The key to the curve fitting method is to do a series of mass loading rates on the filter, and establish the relationship between measured reflectance and mass on the filter paper. This measured relationship should match the Hapke equations which describe theoretically the reflectance as a function of the optical depth. To link the observed and theoretical
reflectance behavior, we must describe the optical depth in terms of mass per unit area on the filter paper.

The reflectance of a finite layer of particles depends on the thickness of the layer and the reflectance of the underlying layer of particles, which is assumed to be of infinite thickness. The optical thickness of a finite layer is defined as (Hapke, 1993)

$$\tau_o = \int_{-}^{\infty} E \, dz$$  \hspace{1cm} (44)

in which $z$ is the altitude and $E (=S+K)$ is the extinction coefficient defined by

$$E = N_e \sigma Q_E$$  \hspace{1cm} (45a)

$$S = N_e \sigma Q_S$$  \hspace{1cm} (45b)

$$K = N_e \sigma Q_A$$  \hspace{1cm} (45c)

where $\sigma$ is the projected cross sectional area of the particle. For nonspherical particles, the area is considered to be the average projected area when the particle is considered at all possible orientations. $Q_e$ is the extinction efficiency, which equals unity ($Q_e = 1$) for closely packed particles which are large relative to the wavelength ($\pi D >> \lambda$). $N_e$ is the effective number of particles per unit volume, which is given by (Hapke, 1993).
where \( N \) is the particle density (particles per unit volume) and \( \phi \) is the filling factor (the fraction of total volume filled with particles), which is equal to \( 1 - \) porosity. Equation 46 is valid for any particle spacing and size distribution.

Incorporating Equation 45 in Equation 44 and integrating yields

\[
\tau_0 = z_0 N_k \sigma
\]  

(47)

where \( z_0 \) is the vertical thickness of the layer. The mass of a particle, \( \sigma_m \), can be related to the cross sectional area of the particle, \( \sigma \), when the area is given by

\[
\sigma = \frac{\pi D^2}{4}
\]  

(48)

and the mass of the same particle is given by

\[
\sigma_m = \frac{\pi \rho D^3}{6}.
\]  

(49)

Hence,

\[
\sigma = \frac{3 \sigma_m}{2 \rho D}.
\]  

(50)

Substituting Equations 46 and 50 into Equation 47 yields

\[
\tau_0 = \frac{-3 z_0 N \sigma_m \ln(\phi)}{2 \rho D \phi}
\]  

(51)
The mass of particles per unit area, $X_m$, is calculated from the thickness of the layer and given by

$$X_m = z_0 N \sigma_M$$  \hspace{1cm} (52)

and Equation 51 becomes

$$\tau_0 = \frac{-3\ln(\phi) X_m}{2 \rho D \phi}.$$  \hspace{1cm} (53)

Equation 53 allows us to write the optical depth in terms of mass loading ($\tau_0 = f(X_m)$), an easily measureable quantity. This enables us to curve fit theoretical reflectance equations (Equation 36) to measured values of reflectance and mass loading rate. The introduction of the filling factor, $\phi$, in Equations 46 and 53 takes into account variability in packing density, particle spacing, and size distribution. Except for $X_m$, the parameters on the right hand side of Equation 53 may be taken as constants for a layer of uniform, homogeneous particles (assuming $Q_\phi$ is equal to a constant: unity). Later, the filling factor, $\phi$, as a function of $z$ will be considered. The variation of $\phi$ with $z$ is a possibility when the particles are filtered onto a filter paper under vacuum. The porosity of the upper-most particles (under atmospheric pressure at the surface) may be higher than the underlying particles which
are at high vacuum pressures. Grouping the constant parameters together in Equation 53, we define a new parameter, $E_M$, as

$$E_M = \frac{-3\ln(\phi)}{2 \rho D \phi}$$

(54)

so that

$$\tau_0 = E_M X_M.$$  

(55)

$E_M$ has units of area per mass. Values of $E_M$ will be a maximum for loosely packed, small, low-density particles and a minimum for tightly packed, large, high density particles.

The Significance of $E_M$

In this Chapter, the value of $E_M$ (in addition to the value of $\gamma_u$) is determined by curve fitting. The value of $E_M$ tells us the number of particles per unit volume of the layer. If we consider a layer of one type of uniform particles with known (or estimated) particle size and mass density, the value of $E_M$ may be used to calculate the filling factor, $\phi$ by rearranging Equation 54 to the form:

$$\frac{\ln \phi}{\phi} = -\frac{2 \rho D E_M}{3}$$

(56)

Hence, the filling factor, may be calculated iteratively for a value of $E_M$ (determined from a best fit curve). Once the filling factor is
known, we calculate the number of particle per unit volume, N, which is given by
\[ N = \frac{\Phi \rho}{\sigma_M} \]  
(57)
or substituting for \( \sigma_M \) (Equation 49) we have
\[ N = \frac{6 \phi}{\pi D} \]  
(58)
The significance of \( E_M \) is that it enables us to calculate N, which, in turn, allows us to convert the scattering and absorption functions for individual particles (which are all derived from the value of \( \gamma_u \)) into the volume extinction, E, scattering, S, and absorption, K, coefficients by using Equations 45a, 45b, and 45c. Equations 46 through 58 all assume that \( Q_t = 1 \), and are only valid for large \( (X, >> 1) \), closely packed particles in which diffraction may be neglected.

Converting the Coefficients in Terms of Water Depth

The extinction, scattering, and absorption coefficients given by Equations 45a, 45b, and 45c have units of 1/length, where length represents the distance within the layer of particles. If we wish to convert this distance, \( d_{\text{layer}} \), to the corresponding distance in the water sample, \( d_w \), which was filtered, we note that
Hence, the coefficients may be written in terms of depth of water sample by multiplying the coefficients calculated in Equations 45a, 45b, and 45c by the factor \( \frac{TSS}{N\sigma_{M_i}} \). Once the coefficients are written in terms of depth of water, they may be expressed in terms of mass of sediment by multiplying by their associated TSS value.

Another interpretation of \( E_M \) is derived by comparing Equations 44 and 55. Since \( \tau_0 = E z_0 \) and \( \tau_0 = E_M X_M \), then \( E_M \) is equivalent to the ratio of the optical depth, \( \tau_0 \), to the mass loading rate (mass depth). In other words, \( E_M \) represents the extinction per mass of sediment per unit area. Hence, \( E_M \) may be considered as the specific extinction coefficient. Multiplying \( E_M \) by the scattering efficiency, \( Q_s \), yields the specific scattering coefficient, and multiplying \( E_M \) by the absorption efficiency, \( Q_a \), yields the specific absorption coefficient.
Hapke Reflectance Model of TSS on a Filter Paper

We now apply the modified Hapke reflectance model to dried TSS on a filter paper. By writing the optical thickness, $\tau_0$, in terms of mass loading rate (mass of sediment per unit area), we may directly utilize data from the typical TSS analysis to determine the $w$ function and other optical parameters of the TSS particles. The key to doing this lies in measuring the reflectance of a series of mass loading rates. We vary the thickness of sediment on the filter paper and measure the corresponding reflectance for each thickness (quantified in terms of mass per unit area). Hence, we establish the relationship between reflectance and mass loading rate. This relationship should match the modified Hapke bidirectional reflectance model (Equation 36). Values of the primary optical parameters of the model are determined by nonlinear least squares curve fitting. We now apply this technique to three water sediments, algae, river sediments, and bacteria.

The Modified Hapke Reflectance Model Applied to Algae

We measured the reflectance of a pure algal culture of *Chlamydomonas reinhardtii*. This species was selected due to its nearly spherical (equant) shape and narrow size distribution. The
volume of individual cells ranges from 55 to 86 $\mu$m$^3$, which corresponds to a diameter range of 4.7 to 5.5 $\mu$m. Pure algal cells were isolated from liquid suspension on tared and precombusted glass fiber filters (Whatman GF/F, 0.7 $\mu$m) by vacuum filtration. Total suspended solids analysis of the algae was done using *Standard Methods for the Examination of Water and Wastewater* (Greenberg *et al.*, 1992). The drying temperature was reduced to 60 C (for one hour) to prevent breakdown of proteins.

Relative reflectance of the algae was measured with a Colortron II (*LightSource, Inc.*, Larkspur, California) which has a bandwidth of 10 nm (from 390 nm to 700 nm), an incidence angle, $i$, of $\pi/4$, an emergence angle, $e$, of 0, and a phase angle, $g$, of $\pi/4$. Relative reflectances were measured for a series of masses of algae on filter paper, ranging from 0 to about 4 g/m$^2$. Each filter paper containing a known mass of algae was scanned four times, and the mean reflectance value was used to curve fit the theoretical equation.

The effect of mass loading rate on relative reflectance for visible wavelengths is shown in Figures 6.6, 6.7, and 6.8. Figure 6.6, which shows reflectance as a function of wavelength, demonstrates the
Figure 6.6. Reflectance and wavelength of algae for various masses on filter paper (area of filter = 0.0015 sq. m).
Figure 6.7. Reflectance and mass loading rate of algae for selected wavelengths.
Figure 6.8. Reflectance, wavelength, and mass loading rate of algae.
absorption bands of chlorophyll near 440 nm and 670 nm. As algal mass is increased, the reflectance decreases (darkens) at all wavelengths, because the underlying white filter paper is being covered with algal cells. The relationship between reflectance and mass loading rate is shown in Figure 6.7 for various wavelengths. The curves vary in shape, from almost linear for nonabsorbing wavelengths (550 nm and 700 nm) to exponential shapes for the absorbing bands (450 nm and 670 nm). The data in Figure 6.7 are used for curve fitting. We note that simple empirical equations are not robust enough to account for the wide variety of shapes exhibited by all of the various wavelengths in Figure 6.7. Figure 6.8 is a 3-dimensional plot of the observed reflectance, mass loading, and wavelength relationship for the *Chlamydomonas reinhardtii*. From Figures 6.6, 6.7, and 6.8, we observe that as $X_M$ is increased, the reflectance approaches an asymptotical value which is associated with color of an opaque (optically thick) layer of algae. The rate of this approach towards an asymptote (derivative of reflectance with respect to $X_M$) depends on wavelength due to the presence of absorption bands. We also note that we are not able to obtain an opaque layer of algae due to the fact that we are
limited by the method of filtration which leads to clogging of the filter and the exceptionally long filtering times associated with large values of $X_M$.

**Curve Fitting and Parameter Estimation**

**Algae**

The reflectance-$X_M$ data as presented in Figure 6.7 was used to obtain parameter values of Equation 36. Equation 36 is made up of two parts, the singly and multiply scattered components defined by Equations 37 and 38. We note that the value of $\tau_0$ in Equations 37 and 38 is redefined using Equation 55 ($\tau_0 = E_M X_M$) in order to express the optical depth in terms of mass loading rate. The adjustable parameters of Equation 36 are the albedo factor of the upper layer, $\gamma_u$, and $E_M$. Nonlinear least squares (NLS) curve fitting was done using *Table Curve 2D* (AISN Software Inc.). The algorithm uses the Levenberg-Marquardt method, which minimizes the sum of squared residuals. Figures 6.9 and 6.10 show the results for wavelengths of 450 nm (absorption band) and 550 nm (non-absorption band), respectively. The curve fitting was done for all 32 bands of reflectance-$X_M$ data for the algae. Figure 6.11 shows the the best values of the albedo factor, $\gamma_u$, as a function of
Figure 6.9. Hapke model fitted to reflectance of algae at 450 nm.
Figure 6.10. Hapke model fitted to reflectance of algae at 550 nm.
Figure 6.11. Albedo factor of algae for isotropic and fitted phase functions.
wavelength. Two different phase functions are compared in Figure 6.11, isotropic ($p(g)=1$) and $p(g) = \text{adjustable parameter}$, in which $p(g)$ is added as a third parameter (in addition to $\gamma_u$ and $E_m$) and allowed to vary between $1-\cos g$ (forward scattering) and $1 + \cos g$ (backscattering). The adjustable phase function curve, shows more relief (higher peaks and lower valleys) than the flatter isotropic curved for absorbing wavelengths (450 nm to 670 nm). Given the values of $\gamma_u$ from Figure 6.11, the relative reflectance of an infinite layer of algae (Figure 6.12) may be calculated by using Equations 28 and 31. The lines in Figure 6.12 correspond to the asymptote of reflectance for each wavelength.

The values of the particle single-scattering albedo, $w$, for various phase functions are shown in Figure 6.13. These values are calculated from Equation 6.12 for the values of $\gamma_u$ which produce the least sums of the square residuals. Because the algae cells are relatively large relative to wavelength, the values of $w$ represent the scattering efficiency, $Q_s$. We also note that $1-w$ equals the absorption efficiency, $Q_a$. The ESPAT function, $W$, which represents the ratio of $Q_a$ to $Q_s$ is shown in Figure 6.14. The effect of phase function on the ESPAT function is shown in Figure 6.15. Values of
Figure 6.12. Modeled reflectance of an infinite layer of algae.
Figure 6.13. Effect of phase functions on $w$ function for algae.
Figure 6.14. ESPAT function for algae (isotropic phase function assumed).
Figure 6.15. Effect of phase function on ESPAT function for algae.
W are very sensitive to the value of the phase function. The internal absorption coefficient, \( \alpha \), for the algal cells is shown in Figure 6.16. Values of \( \alpha \) are equal to \( W/2D \), where \( D \) is the mean diameter of the individual algal cells. The absorption coefficient may only be calculated using this relationship when \( w>0.25 \) (Hapke, 1993), which is the case at all wavelengths for the algae (Figure 6.13).

The F Statistic, which represents how well the model fits the data is shown in Figure 6.17 for various phase functions. The critical F value for this data set (2 parameters and 6 data points) is 6.94 (0.05 level). The numerator degrees of freedom is 1 (the number of parameters minus one) and the denominator degrees of freedom is 4 (=6-2). The best fits occur at 440 nm, where the chlorophyll absorption band occurs at small wavelengths. It is in this wavelength region (blue), where the assumption that the particles are much larger than the wavelength is most appropriate.

Figure 6.18 shows that inclusion of a term for the opposition effect does not change the best fit values of \( w \). The opposition effect is negligible at the relatively large phase angle of \( \pi/4 \). Figures 6.19 and 6.20 show the effect of adding an exponent, \( \beta \), (a
Figure 6.16. Internal absorption coefficient for algae ($D = 5$ microns) based on ESPAT function with isotropic phase function.
Figure 6.17. F-statistic of various phase functions for algae.
Figure 6.18. w function and the opposition effect of algae \((g = \pi/4)\).
Figure 6.19. Exponent on mass loading term of best fit for algA using 3 different reflectance models.
Figure 6.20. Effect of mass exponent on w function for algae.
third adjustable parameter) to the mass loading term, $X_m$, the Hapke bidirectional reflectance model (Equations 36, 37, and 38). Introduction of the $\beta$ term does, in fact, increase the F Statistic. Values of $\beta$ range from 0.8 to 1.0 (Figure 6.19), which are in agreement with the exponent of organic sludges obtained by Lo (1971). However, introduction of $\beta$, also dramatically alters the values of the other adjustable parameters of the Hapke model as shown in Figure 6.20. Figure 6.21 shows values of the other adjustable parameter, $E_m$, with respect to wavelength. The values of $E_m$ may be used to determine the filling factor for the algae on the filter paper by using Equation 54. For an assumed particle density of 1.0 and a particle size of 5 $\mu$m, the filling factor is, on average, about 0.45, corresponding to a porosity of 0.65.

**Mississippi River TSS**

We now apply the Hapke bidirectional reflectance model and the above curve fitting technique to Mississippi River TSS. The sample was collected during spring flood stage at the east levee near downtown Baton Rouge, the measured TSS value was 70 mg/L. The theoretical and observed reflectance-$X_m$ relationships for 450 nm is shown in Figure 6.22. The albedo factor (Figure 6.23), $w$ function
Figure 6.21. Specific extinction, scattering, and absorption coefficients for algae.
Figure 6.22. Hapke model fitted to reflectance of Mississippi River TSS at 450 nm.
Figure 6.23. Hapke's albedo factor of Mississippi River TSS.
(Figure 24), ESPAT function (Figure 6.25), efficiencies (Figure 26), specific extinction coefficient (Figure 6.27), and specific absorption-scattering coefficients (Figure 6.28) of the Mississippi River TSS are shown in Figures 6.23 - 6.28. As with the algae, values of the coefficients are highly sensitive to the type of model (diffusive or bidirectional) and the assumed phase function. Figure 6.26 shows that at wavelengths of 400 nm the river particles absorb 30 percent of the incident power and scatter 70 percent. As the wavelength increases, the extinction of light radiation is dominated by scattering, which approaches 100 percent of extinction at 700 nm. The isotropic extinction coefficient in Figures 6.27 and 6.28 increases with wavelength. This suggests that the extinction efficiency is a function of wavelength. The increase in extinction increases with wavelength may indicate that diffraction is occurring at the longer wavelengths (greater than 500 nm) where the assumption about large particles relative to wavelength is not valid. At wavelengths less than 500 nm, the specific extinction is independent of wavelength (with slope of zero) and equal to about 0.4 m²/g. At wavelengths near 700 nm, the specific extinction value is approaching 0.8, which is twice that of the extinction at
Figure 6.24. Hapke's $w$ function of Mississippi River TSS.
Figure 6.25. Hapke's ESPAT function of Mississippi River TSS for isotropic phase function.
Figure 6.26. Scattering and absorption efficiencies of Mississippi River TSS.
Figure 6.27. Specific extinction coefficient for various phase functions of Mississippi River TSS.
Figure 6.28. Specific extinction, scattering, and absorption coefficients for Mississippi River TSS.
450 nm, as would be expected if diffraction plays a role in extinction ($Q_e = 2$ with diffraction).

**Bacteria**

A sample of bacteria from an activated sludge wastewater pond was collected from a chemical plant. The reflectance-$X_m$ relationship of the filtered and dried bacteria is shown in Figure 6.29 for 450 nm. Figures 6.30 through 6.35 show the albedo factor, $w$ function, ESPAT function, efficiencies, specific extinction, and specific absorption-scattering coefficients, respectively. Figure 6.33 shows the absorption peak at 410 - 420 nm, which agrees with published values of the peak at 415 nm for bacteria (Demers, 1991). Figure 6.35 shows the specific extinction behavior similar to that of the river sediments, in that the extinction increases (linearly) with wavelength beyond 440 nm. This indicates that the region of diffraction occurs at wavelengths above 440 nm and that the assumption that $Q_e = 1$ is only valid for wavelengths below 440 nm. The wavelength at which the derivative of the specific extinction function goes from zero to positive is shifted from 500 nm for the river sediments (Figure 6.22) to 440 nm for the smaller...
Figure 6.29. Hapke model fitted to reflectance of bacteria at 450 nm.
Figure 6.30. Albedo factor of bacteria for three different reflectance models.
Figure 6.31. $w$ function of bacteria for three different reflectance models.
Figure 6.32. ESPAT function of bacteria for three different reflectance models.
Figure 6.33. Scattering and absorption efficiencies of bacteria.
Figure 6.34. Specific extinction of bacteria for three different reflectance models.
Figure 6.35. Specific extinction, scattering, and absorption coefficients for bacteria.
bacteria. Hence, the wavelength at which there is a change in slope may be related to the size of particles.

Summary of Three Sediments

Figures 6.36, 6.37, 6.38, and 6.39 show the reflectance of an infinite layer, the \( w \) function and the \( W \) function for the algae, river sediments and bacteria. The specific extinction coefficients are shown in Figures 6.40 - 6.42. Although the color, absorption, and scattering properties are very similar for the bacteria and the river sediments, their absorption and scattering properties may be distinguished based on their mass extinction coefficients. The bacteria, on the order of 1 \( \mu \)m in size, exhibit much greater absorption and scattering on a mass basis than the larger sized algae and river sediments. sediments, their absorption and scattering properties may be distinguished based on their mass extinction coefficients in Figure 5.40. The \( w \) function in Figure 5.38 shows that in the spectral region near 550 nm, where the algae do not absorb significantly, all three particulate populations scatter the same ratio of light relative to extinction (90 percent). The absorption peak of bacteria at 410 nm is visible in Figure 5.39 and Figure 5.41.
Figure 6.36. Relative reflectance of an infinite layer of algae, Mississippi River TSS, and bacteria.
Figure 6.37. Albedo of algae, Mississippi River TSS, and bacteria (isotropic phase function).
Figure 6.38. $w$ function of algae, Mississippi River TSS, and bacteria (isotropic phase function).
Figure 6.39. ESPAT function of algae, Mississippi River TSS, and bacteria (isotropic phase function).
Figure 6.40. Specific extinction coefficient for algae, Mississippi River TSS, and bacteria.
Figure 6.41. Specific absorption coefficient for algae, Mississippi River TSS, and bacteria.
Figure 6.42. Specific scattering coefficient for algae, Mississippi River TSS, and bacteria.
Conclusions

Hapke's bidirectional reflectance model, modified to include mass loading, is shown to adequately model the reflectance-mass loading rate relationship of these three diverse sediment samples. The Hapke model permits measurement of several optical parameters by simple, reflectance spectroscopy techniques. Because the phase function greatly affects the parameter values, all parameters should be defined with the associated assumed or measured phase function. Nonlinear least squares curve fitting enables estimates of the single particle-scattering function (w), the ESPAT function (W), and the internal absorption coefficient (α).

This is the first time that these parameters have been measured for TSS. Hence, we are able to rigorously quantify the absorption and scattering properties of algal cells, Mississippi River TSS, and bacteria by using simple and quick analytical techniques based on the traditional TSS analysis.
CHAPTER 7. HAPKE REFLECTANCE MODEL PARAMETERS AND REMOTE SENSING ALGORITHMS

This Chapter discusses the relationship of the Hapke reflectance model parameters to remote sensing algorithms of total suspended solids (TSS) in natural waters. Combining the Hapke reflectance model with the traditional TSS analysis, we have developed a convenient means of measuring a number of optical properties of TSS. The Hapke reflectance model parameters expressed in terms of mass of sediment, as derived in Chapter 6, provide a means of measuring parameters which are typically estimated by curve fitting of remotely sensed reflectance and TSS data. The Hapke model parameters are suitable for the widely used, quasi-theoretical, remote sensing algorithm of Stumpf and Pennock (1989). We also propose a conceptual model, based on dimensional analysis, which provides a simple means of interpreting remotely sensed reflectance values. Reflectance spectroscopy should be applied to TSS during groundtruthing data collection. The additional attributes of absorption and scattering functions of TSS are easily obtained and provide useful information for
interpreting the remotely sensed reflectance of the many new satellite color sensors at various wavelengths.

The Asymptote of Remotely Sensed Reflectance

Researchers have presented many different models to describe the relationship between remotely sensed values of reflectance, R, and suspended sediment concentrations. The function of R versus TSS has been modeled as linear (Munday and Alfoldi, 1979), logarithmic (Stumpf, 1988), power (or log-log) (Violler and Sturm, 1984), and logistic (Munday and Alfoldi, 1979, Stumpf and Pennock, 1989). Nonlinear models give higher correlation coefficients than linear models (except for small ranges of concentration which may fit a linear model).

Quasi-Analytical, Logistic Models

Munday and Alfoldi (1979) and Stumpf and Pennock (1989) applied a radiative transfer model of a logistic form to the Reflectance-TSS relationship and found that the model predicted an asymptotic value. This asymptotic behavior was corroborated by Schiebe et al. (1992) and Lodhi et al. (1997). Schiebe et al. (1992) found the exponential relation to best model a 12 year long data set which covered a large range of TSS values and seasonal
conditions in Lake Chicot, Arkansas. This is in contrast to other researchers who used linear regressions to model reflectance over a single season or date (with correspondingly small range of TSS values). Schiebe et al. (1992) found it difficult to separate the differing contributions of backscatter from suspended sediments and backscatter from phytoplankton at low suspended sediment levels. They found that they had to model the relationship between $R$ and TSS separately above and below 25 mg/L. This is because above 25 mg/L inorganic sediments dominated, whereas below 25 mg/L factors other than inorganic particulates contribute significantly to the reflectance signal (Schiebe et al., 1992). This gives an indication that the color of sediments is a function of TSS values, ranging from phytoplankton color at low TSS to inorganic color at high TSS values for this particular water body. The wide variety of possible TSS colors requires a robust modeling approach which incorporates the inherent absorption and scattering properties of TSS, not just the values of TSS alone.

The logistic models are based on the radiative transfer model developed by Gordon et al. (1975) for an optically deep and
homogeneous water column. The reflectance, $R_\infty$, just above the water surface is given by:

$$R_\infty = \frac{y'b_b}{a + b_b}$$  \hspace{1cm} (1)

where $a$ is the absorption coefficient of water, and $b_b$ is the backscatter coefficient, $y'$ is a constant $= 0.33/ (m^2 T_w)$; where $m$ is the refractive index of seawater and $T_w$ is the transmission through the water surface. For turbid water, Equation (1) becomes (Stumpf and Pennock, 1989)

$$R_\infty = \frac{y' F_s}{1 + \frac{G_s}{n_s}}$$  \hspace{1cm} (2)

where $n_s$ is the sediment concentration; $y' = 0.178$; $F_s = b_{bs}^s / s^s$; $G_s = a_s^s / s^s$; $s^s = b_{bs}^s + a_s^s$; $b_{bs}^s$ is the specific backscatter coefficient for the sediment; $a_s^s$ is the specific absorption coefficient for sediment; $a_x$ is the absorption for non-sediment constituents, including water ($a_w$), dissolved pigments ($a_d$) and chlorophyll ($a_c$; $a_c = a_{ch}^c n_c$ where $a_{ch}^c$ is the specific absorption coefficient for chlorophyll and $n_c$ is the chlorophyll concentration). Chlorophyll, despite being a particulate pigment, is separated from the particulates and grouped with the dissolved constituents during this approach. Coefficients ($F_s$ and $G_s$)
in Equation 2 are estimated by using a non-linear curve fitting or by linear regression after rewriting Equation (2) into the relationship $1/R_\infty$ versus $1/n_s$ (Munday and Alfoldi, 1979). Stumpf (1992) reported values of $F_s$ ranging from 0.24 (Delaware Bay) to 0.41 (Mobile Bay) and values of $G_s$ ranging from 21.0 (Mobile Bay) to 26.4 (Delaware Bay) for small, short-term data sets.

Equation 2 provides coefficients which can be interpreted in context of the materials in the water (Stumpf, 1992). The relationship between $R_\infty$ and TSS may change with algal blooms or with large changes in the grain-size of the sediment. The variable $G_s$ is directly affected by pigments such as chlorophyll through $a_\infty$, where $a_\infty$ is linearly proportional to the concentration of pigments. Thus determinations of pigment concentrations can be incorporated into Equation 2.

As $n_s$ approaches infinity, Equation 2 predicts that the reflectance value approaches the asymptote given by

$$\lim_{n_s \to \infty} R_\infty = \frac{v' b'_s}{a'_s + b'_m}$$

An inherent assumption of this equation and its respective asymptote is that at very high values of TSS the inorganic
particulates dominate the reflectance signal and the chlorophyll signal is entirely ignored. Although this is reasonable for some natural bodies of water, it is not universally valid (e.g. during an algal bloom). Another important point to consider with respect to Equation 2 is that the values of $F_s$ and $G_s$ are model coefficients, they are parameters which are fitted to the data set and they are not physically measured. The method described in Chapter 6 may provide a measurement technique for tightly packed TSS, where the value of the reflectance of an infinite layer serves as a dry asymptote.

**Linear Models**

To develop a remote sensing model which uses the actual, measured color spectra of TSS, it might be more appropriate to use a model which does not separate chlorophyll from the particulate optical properties. Morel and Prieur (1977) developed a linear model which calculates diffuse reflectance starting with:

$$ R = 0.33 \left( \frac{b'}{a} \right) (1 + \Delta), $$

(4)

where $R$ is the reflectance just beneath the water surface, $\Delta$ is a corrective term which depends on the radiance distribution and
the volume scattering function, $a$ is the absorption coefficient: $a = a_w + a_y + a_p$ (for water molecules, yellow substance, and particles) $b'$ is the backscattering coefficient: $b' = b'_p + b'_w$ (for particles and water molecules).

A Simple Remote Sensing Model based on the Reflectance Spectra of Dried Total Suspended Solids

Prior to development of the method presented in the Chapter 6 it had not been easy to measure the specific backscattering and absorption coefficients for particulates. We now present a model based on measuring the specific backscattering and absorption coefficients of TSS. It is similar in form to Equation 4 above. Although its form is linear, any nonlinearities will be inherently contained in the values of the measured coefficients. A unique value of $b$ and $a$ is measured for each TSS sample.

$$R = \alpha \left( \frac{b'_w + b'_p \cdot n_s}{a_w + a_y + a_p \cdot n_s} \right)$$

The advantage of Equation 5 is that all of the variables on the right hand side are easily measureable. In fact, only three simple laboratory measurements are required to explain how water constituents contribute to a remotely sensed reflectance. They are the 1) absorption spectrum of the dissolved constituents (the
filtrate passing through the filter), 2) TSS analysis, and 3) reflectance of TSS (which only adds about 30 seconds to a TSS analysis). From these three simple measurements the value of \( \alpha \) may be determined for given body of water. A remote sensing algorithm based on Equation 5 is well suited for low cost remote sensing projects which do not have access to expensive optical equipment and extensive data acquisition.

**Dimensional Analysis of Water Reflectance**

To give insight into the relationship between the variables we conduct a dimensional analysis. The resulting dimensionless equation and variables will indicate insightful dimensionless numbers, which will be used to classify water bodies based on their optical properties. This approach will be helpful in determining how the optical measurements of the particulates relate to remotely sensed values of reflectance.

We start with the functional equation for water reflectance containing all significant variables

\[
R = f(a_d, b_d', a_s^*, b_s^*, n_s)
\]  

(6)

where \( a_d \) is the absorption coefficient for all dissolved constituents.
and $b_d'$ is the backscattering coefficient for all dissolved constituents. In this case, we have expressed variables as either dissolved or solid. Then $b_d'$ is due entirely to the water molecule (yellow substance does not scatter light) and is a known constant value. Hence, we remove the $b_d'$ variable since it is taken as a constant and are left with

$$R = f(a_d, a_s^*, b_s^*, n_j)$$

in which $[R] = \text{dimensionless}$

$$[a_d] = 1/L$$
$$[a_s^*] = L^2/M$$
$$[b_s^*] = L^2/M$$
$$[n_j] = M/L^3$$

All of the independent variables (right hand side) are easily measured in the laboratory with simple instruments. In this case we are defining the absorption and backscattering coefficients of the particulates based on mass (mass loading on filter paper) and not on the depth of water sample (See Chapters 5 and 6).

In dimensional analysis, the number of independent dimensionless groups needed to correlate the variables in the reflectance process is equal to the number of variables (5 in this
case) minus the number of basic dimensions (2 in this case: length and mass). Hence we require 3 basic groupings of variables to correlate experimental results (Buckingham, 1915). We begin by eliminating the dimension of mass, so Equation (7) becomes:

$$R = f_1(a_d, a_s, b_s, n_s)$$

Then we eliminate the dimension of length to obtain:

$$R = f_2\left(\frac{a_s \cdot n_s}{a_d}, \frac{b_s \cdot n_s}{a_d}\right)$$

Equation (9) may be used to define dimensionless numbers or to fit remotely sensed values of reflectance to simple laboratory measurements.

**TSS in Water and On a Filter Paper**

There are obviously optical differences between the TSS in the water column and dried on a filter paper. Two significant differences are the particulate spacing and the refractive index of the background medium (water and air). For TSS in the water column (*in-situ*), the particles are dispersed and imbedded in water with refractive index of 1.33. In this Dissertation we isolate the TSS on a filter paper under vacuum resulting in a closely packed layer of particles. The particles are dried in an oven to
remove any water and dessicated to room temperature. Hence, the particles are imbedded in a matrix of air with refractive index of about 1.

As discussed in Chapter 6 and Hapke (1993), the most significant optical change in going from dispersed (isolated) to concentrated particles is the loss of scattering due to diffraction. Isolated particles surrounded by air (or water) have an efficiency of 2 ($Q_e=2$) and diffract light near their edges resulting in forward scattering. Concentrated particles in contact with neighboring particles, on the other hand, have an efficiency of 1 ($Q_e=1$) and do not diffract significant visible light. In the absence of diffraction, they do not exhibit the strong forward scattering, but rather scatter light isotropically.

Another difference between what is going on in the water column and on the filter paper, is the role of multiple scattering. By bringing the TSS particles in close contact we are increasing the number of times a given photon is scattered. Light reflected from one particle is much more likely to encounter another particle when they are in close contact. Fortunately, the Hapke theory takes these multiple scatterings into account, not only between
particles, but also between and within the filter paper. A major weakness of previous filter pad techniques has been the inability to theoretically quantify the multiple scattering between the sediments and the filter paper.

The optical parameters of TSS measured with reflectance spectroscopy and the Hapke theory should be very closely related to the actual in-situ values within the water column. This may or may not be a linear relationship. The main difference should be in diffraction which increases as TSS decreases. Another complication is the different refractive indices of the imbedding matrix. Future work will provide the relationship between scattering and absorption coefficients measured in the water column and on a filter paper.
CHAPTER 8. CONCLUSIONS

A review of the Literature shows that there is currently no standard method for measuring the color and optical properties of total suspended solids (TSS). The contribution of TSS to water color and remote sensing algorithms is poorly understood. Few simple techniques are available for measuring the absorption and scattering properties of TSS.

In this Dissertation, reflectance spectroscopy and radiative transfer theory were applied successfully to TSS on a filter paper, to measure their color, extinction, absorption, and scattering of visible light. Optical differences in TSS are now quantifiable. The new, theoretically based technique provides a simple means of comparing TSS from different locations and times. The method is conveniently linked to the traditional TSS analysis by adding one additional step, the measurement of reflectance. The bidirectional reflectance model of Hapke (1993) for a finite layer of particles is modified to include the typical TSS measurement of dry mass. Reflectance measurements of a series of different dried masses on
filter the paper enables prediction of the reflectance of a layer of infinite thickness by the Hapke model.

The twelve specific conclusions are listed below.

1. Hapke's bidirectional reflectance model, modified to include mass loading, is shown to model the observed reflectance-mass loading rate relationship for algae, river sediments, and bacteria. The shape of absorption and scattering functions agrees with measurements obtained by other researchers.

2. A 10 nm bandwidth provides adequate spectral resolution to measure the chlorophyll absorption bands of algae. A 10 nm bandwidth spectrophotometer gives very similar reflectance spectra to a 2 nm bandwidth instrument at one tenth the cost. The main advantage of the lower cost instrument is convenience of use.

3. The reflectance-mass loading rate relationship for a series of finite sediment layers enables measurement of the specific extinction, absorption, and scattering coefficients of TSS as functions of wavelength.

4. Although the Kubelka-Munk and Hapke model fit the observed data equally well, the bidirectional Hapke model provides meaningful parameter values which are linked to the fundamental
optical properties of TSS. The Kubelka-Munk theory assumes a
diffusive distribution of incident and emergent light, whereas, the
Hapke model takes the geometry of incidence and emergence into
account. One advantage of the Kubelka-Munk model is its
simplicity.

5. The CIE XYZ coordinates are easily calculated from the modeled
reflectance of an infinite layer. The color of TSS is not very
sensitive to oven temperature and duration. TSS may now be
assigned a Munsell color value.

6. Several optical parameters have been measured for TSS for the
first time. These include the albedo, particle single-scattering
albedo (w) function, effective single-particle absorption-thickness
(espat) function, extinction, absorption, and scattering efficiencies.
The parameters permit optical classification and comparison of TSS
from different locations or times. The approach is a first step in
obtaining the independent, inherent optical attributes of TSS in
terms of their mass.

7. Although the bacteria and Mississippi River TSS have almost
identical reflectance functions (color) for an infinite layer, their
respective specific coefficients are significantly different.
8. Values of the calculated optical parameters are sensitive to the phase function, which was assumed isotropic in this work.

9. The scattering and absorption coefficients of TSS particles dried on a filter paper differ from TSS in the water column. The differences are due to the role of diffraction, particle spacing, multiple scattering, and the refractive index of the media in which the TSS are imbedded.

10. The scattering properties of algae, which are often ignored in remote sensing algorithms, are measured and significant.

11. The bacteria exhibit very high specific extinction, absorption, and scattering coefficients relative to algae and river sediments due to their small size and low mass density.

12. The Hapke model enables us to account for multiple scattering within and between the TSS particles and the filter paper. Previously, this quantity was based on a correction term.

13. The new method enables quantification of the packaging effect of algae.
CHAPTER 9. RECOMMENDATIONS AND APPLICATIONS

A number of applications and future research are expected to come out of this Dissertation, which developed a convenient new tool for characterizing total suspended solids. This tool, based on assigning optical attributes to TSS, provides a snapshot in time and space of the particulate population and has applications in Water and Wastewater Analysis, Monitoring and Management of Water Resources, Erosion and Sediment Transport Studies, Remote Sensing, Harmful Algal Blooms Monitoring, and Public Education Efforts. Future research is required to delineate the limitations and usefulness of the experimental and theoretical methods developed in this work.

Future Research

The role of particle size and distribution on optical parameters needs to be quantified on known TSS samples. These may include known clay and silt samples, with a range of pigments. Natural samples of TSS may also be used if their particle size distribution is measured independently.
The significance of the specific extinction coefficient, and its dependence on wavelength, should be studied with regard to TSS particle size, absorption bands, and the role of diffraction.

Relationship between the scattering and absorption coefficients of TSS measured by reflectance spectroscopy in this work should be compared to remote sensing algorithm coefficients, particularly those of Stumpf and Pennock (1989).

The method should be applied on a range of filter pore sizes. In this work only 0.7 μm pore sizes were used. This will enable the absorption and scattering of TSS to be attributed to specific size ranges.

Scattering phase functions should be measured by varying the phase angle, g. This simply requires different light source and detector geometries.

The color and optical properties of TSS should be linked to other water quality parameters for a given watershed. This will improve the relationship between water quality and water color.

Applications

The addition of TSS optical attributes enables all the significant contributors to water color to be measured. Hence, the dissolved
and particulate contributions to absorption and scattering may now be summed to explain water color and remotely sensed reflectance.

Small scale remote sensing applications with a digital camera will enable the linking of TSS color to water color. This would provide a simple monitoring tool, which would be understandable to the general public.

The color of TSS may be used to monitor wastewater ponds and mixed liquor suspended solids. The absorption peak of bacteria at 415 nm is measurable with the new technique.

The specific absorption coefficient may be used to measure chlorophyll a content of natural water samples. The new method enables better estimates of the packaging effect of algae and could replace the use of harmful solvents.

The method should be repeated on Fixed Suspended Solids. The effect of disturbing the layer of particles with high temperature or solvent would have to be considered. The specific absorption coefficients of the FSS may provide a fingerprint for tracing sediments back to their source.
By linking optical properties of TSS to upstream soil colors, the method should be tested as a nonpoint source pollution tracer. The relation between TSS color as a function of various hydrologic regimes should be established for specific watersheds. This could lead to the estimation of stream and river velocity from remotely sensed images of water color, which would be a function of the stage and velocity. The fate of sediment plumes could also be monitored with the new method.

TSS colors of TSS discharged (effluent) at a point source could serve as an optical signature for that TSS in the downstream body of water.

A database of TSS colors should be established by State and Local Environmental Agencies to monitor and manage water color, water quality, and nonattainment areas. The relationship between water quality and water color could be established for various water quality parameters. This database, which could be in the form of a geographic information system, would serve as the basis for the interpretation of future remote sensing images and the identification of seasonal and long term changes in water quality. Water quality goals could become water color goals.
Reflectance spectroscopy should be applied to bottom sediments and bottom vegetation in optically shallow bodies of water.

The new method may be used to measure the changes in the optical properties of TSS due to resuspension of darker bottom sediments. The fact that not all TSS are optically equal has been shown and quantified in this dissertation.

Any time groundtruthing of TSS is done for remote sensing, the new method should be added to the TSS analysis along with dissolved absorption measurement with a spectrophotometer. Hence, all optically active water constituents are now easily and rapidly measureable.

Now that we are able to measure the color of TSS in addition to the traditional dissolved color, we may link the particulate color to the organic content of the TSS, and the dissolved color to dissolved organic matter (DOM). Because partition coefficients of hydrophobic contaminants are measurable in terms of DOM and organic content of the solid phase, then they may also be measureable in terms of the color of water relative to the color of the solids. This would enable prediction of the mobility of hydrophobic contaminants based on water and sediment color.
The new optical attributes of TSS may be used on a global scale to estimate standing crop and production of carbon by phytoplankton.

The color of TSS may be compared to the colors of larger organisms in the aquatic ecosystem. For example, the color of smaller fish and tadpoles relative to the color of TSS would determine their visibility and ultimate survival. Evolutionary influences in coloring could be attributed to the TSS in the native waters of fish. As the color of TSS changes in watersheds over time, the changes in visibility would be expected to change predator relationships.

A number of commercial opportunities are available from the measurement of TSS color. This exact color can be saved and imported into graphic art documents. Hence, the actual color of a certain species of algae or TSS could be used in countless commercial and public education applications. For example, interior and exterior paints could be developed to match a certain TSS color from a certain ocean or river. TSS colored paint would provide camouflage for submerged applications. Natural TSS colors could also be utilized in dyes for clothing.
LITERATURE CITED


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Miller, William L. 1994. Recent Advances in the Photochemistry of Natural Dissolved Organic Matter. in *Aquatic and Surface*


The author was born July 7, 1962, in Elgin, Illinois. He grew up on a small farm on the edge of a glacial outwash plain across the field from where his grandfather's grandparents originally settled in 1848 from Glasgow, Scotland. His great-great-grandfather was almost kicked off the train enroute to Illinois for raising concerns about the welfare of two gentlemen who were in chains in a field in Ohio. The author's parents, both retired farmers, still live on the farm, which was originally home to the Pottawatami people and covered with 12-foot tall big-bluestem prairie grass prior to the arrival of Granddad.

The author has delivered over 7,000 pizzas, with very few of them over two hours late. In 1980 he graduated from Central High School, Burlington, Illinois, where he holds the record for highest, career field goal percentage in basketball (100 percent). He is a former Alumni Fellow and NASA Graduate Researchers Fellow at Louisiana State University. He is president of World Ecologists Ltd., formed in 1992 to work with people and nature for the benefit of both. He has worked as a volunteer with children at
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DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Dean Leslie Muirhead

Major Field: Civil Engineering

Title of Dissertation: Color Measurement and Reflectance Spectroscopy of Total Suspended Solids for Remote Sensing and Environmental Monitoring of Aquatic Ecosystems

Approved:

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Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

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Date of Examination: October 24, 1997

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