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**The relation between spectral reflectance and dissolved organic carbon
in lake water: Kejimikujik National Park, Nova Scotia**

by

Heather D. M. Hirtle

**A thesis submitted to the Faculty of
Graduate Studies and Research in partial fulfillment
of the requirements for the degree of
Master of Arts**

**Carleton University
Ottawa, Ontario
24 April 2001**

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**The undersigned recommend to
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acceptance of the thesis**

**Relation between spectral reflectance and dissolved organic carbon in lake water:
Kejimikujik National Park, Nova Scotia**

**submitted by Heather D. M. Hirtle, B.Sc.
in partial fulfillment of the requirements for
the degree of Master of Arts**

Chair, Department of Geography and Environmental Studies

Thesis Supervisor

Thesis Supervisor

Abstract

Relations between dissolved organic carbon (DOC) concentrations and the spectral reflectance of lake water were examined in Kejimikujik National Park. Spectral reflectance measured from ground and satellite remote sensing platforms was used to create regression models for the prediction of DOC with r^2 values of 0.94 and 0.72 respectively. The location of the peak wavelength of the ground spectral measurements and a cluster analysis of the satellite measurements separated lakes in the park into two distinct groups with different DOC concentrations. An analysis of the potential sources of DOC identified three variables important for the prediction of DOC concentrations within the lake, namely flushing rate, the area of deciduous forest and the area of open land within the watershed ($r^2 = 0.41$). As DOC concentrations were related to mercury concentrations ($r^2 = 0.86$) these models may be used to assist in the identification of lakes that are sensitive to mercury pollution.

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1.0 Introduction

Over the past five years there has been increasing concern regarding mercury concentrations in Atlantic Canada. Increased concentrations are having negative impacts on wildlife in the area, especially on the common loon, as well as posing potential risks to human health (Parks Canada, 1998). A great deal of research has been done in Kejimikujik National Park regarding the sources, fate and effects of mercury within the environment because it is located in an acid-sensitive area downwind from major pollution centres in the northeastern United States and southeastern Canada.

Prior studies conducted in Kejimikujik have helped to identify a positive relation between concentrations of mercury and dissolved organic carbon (DOC) in the lakes within the park (Beauchamp et al., 1997; Clair et al., 1998). Lakes with high concentrations of DOC also tend to have high concentrations of mercury.

DOC is the fraction of total organic carbon (all carbon atoms covalently bonded in organic molecules) in water that passes through a 0.45 µm pore-diameter filter (Wetzel, 1983). DOC concentrations in lakes generally range between 0.5 and 30 ppm (Driscoll et al., 1995; Watras et al., 1995; Cai et al., 1999) but can reach from 30 to 50 ppm in wetlands and marshes (Choi et al., 1998). DOC is a mixture of simple substances such as sugars, fatty acids and alkanes, and of complex polymeric molecules. These have a wide range of molecular weights and are often referred to as humic acids. DOC also contains fulvic acids, which are water-soluble, natural organic substances of low molecular weight that are derived from humus. Fulvic acids are chelating agents that can bind and hold metal ions in solution (Driscoll et al., 1995; Gergel et al., 1999). Tannins are a type of fulvic acid, which consists of any group of phenolic compounds that are

produced by metabolism in trees and plants, and are part of the degradation-resistant materials formed during the decomposition of vegetation. Tannins are found in any water where large quantities of vegetation have decayed and can impart a faintly yellowish to brown colour to the water.

DOC is produced both autochthonously (within the water column) and allochthonously (from terrestrial sources) (Hessen and Tranvik, 1998). Autochthonous DOC is produced by the excretion of extra-cellular material, zooplankton feeding and fecal matter and from release during cell death and decay (Rochelle-Newell et al., 1999). The DOC released via these sources is often colourless, composed of humic acids, and breaks down to carbon dioxide within 48 hours (Gergel et al., 1999).

External sources of DOC include riverine inflows, wetland discharge, release from sediments and airborne inputs (Rochelle-Newell et al., 1999). DOC that originates from terrestrial and marsh vegetation has humic and fulvic acid components, which are products of the degradation of vegetative lignin and cellulose. Fulvic acids are more stable than humic acids and can remain in circulation for months to years. These sources are responsible for imparting a stained colour to the lake water (Wetzel, 1983).

This stained colour alters the optical properties of the lake water, thereby making it possible to identify those lakes with high concentrations of DOC. The observed colour of the water is a direct consequence of the scattering and absorption of incoming radiation (direct solar and diffuse skylight) by the optically-active components that are indigenous to natural waters (Bukata et al., 1997). In comparison with distilled water, the transmission of light through lake water with increasing concentrations of DOC,

particularly fulvic acids, is drastically reduced and the absorption pattern is shifted selectively (Frey, 1966).

Optically-active components of aquatic systems, such as chlorophyll, DOC and suspended sediments, have been studied in ocean water using various remote sensing platforms (Bukata et al., 1995; Kondratyev et al., 1998). Similar studies have been conducted in natural waters (e.g., lakes and rivers), but due to the complexity of these systems most studies focus on measuring chlorophyll (Bukata et al., 1997; Hoogenbloom et al., 1998; Thiemann and Kaufmann, 2000) or suspended sediments (Ritchie et al., 1976; Jorgenson and Edelvang 2000). Literature involving the remote sensing of DOC is limited and what does exist offers little information regarding the interpretation of spectral features, as they often overlap with those caused by chlorophyll or suspended sediments.

Studies by Markager and Vincent (2000) and Arts et al. (2000) predicted concentrations of DOC in individual lakes using the assumption that the concentration of all other optically-active components is minimal. To insure this they measured DOC based on UV attenuation (280-400 nm), as DOC is the major optically-active component at these wavelengths.

Various authors have studied the DOC concentrations in Lake Ladoga, Ontario, and Lake Ontario. Kondratyev et al. (1998) created numerical models for Lake Ladoga using Monte Carlo simulations and in-situ data collected from ship-borne sensors. These models predict the concentrations of chlorophyll, DOC and suspended sediments. Bukata et al. (1997) studied the responsivity of chromaticity coordinates to the presence of the optically-active components. It was found that water with high concentrations of DOC is

brownish in colour and exhibits a dominant wavelength between 560 and 570 nm. Similar studies were also conducted by Pozdnyakov et al. (1998).

Arenz et al. (1996) and Vertucci and Likens (1989) used field portable spectroradiometers to measure the reflectance of lakes in Colorado and the Adirondack mountain region respectively. Both studies used regression analyses to predict DOC concentrations based on spectral reflectance of the lake water.

To predict DOC concentrations various authors have used landcover analyses. The most widely studied landcover class is the proportion of the lake watershed that is covered by wetland (Driscoll et al., 1995; Gorham et al., 1998; Gergel et al., 1999). St. Louis et al. (1995) have shown that wetlands export more DOC per unit area than upland areas within the watershed. Water in streams can exhibit twice the concentration of DOC after passing through a wetland than the water upstream of the wetland (Wetzel, 1983). Catchment slope (D'Arcy and Carignan, 1997) was also determined to be a factor in the determination of DOC concentrations when landcover and geology are constant throughout the study area. Vegetation type plays an important role in predicting DOC concentrations as deciduous forest has been found to produce higher concentrations of phenolic acids (e.g., fulvic acids) than coniferous forest (Dahlgren and Singer, 2001). D'Arcy and Carignan (1997) also found a weak relation between DOC and the area of coniferous forest within a watershed as the concentration of DOC measured in soils under coniferous forests is often higher than that measured in soils under deciduous forests (Khomotova et al., 2000).

The purpose of this project is to determine whether it is possible to predict the concentration of DOC within a lake using two different procedures. The first deals with

the prediction of DOC using different remote sensing platforms, ground and satellite, to measure the spectral properties of the lake water itself. The second objective involves identifying and utilizing the potential sources of DOC to predict the concentration of mercury within the lake. This project will test methods that can be used for the identification of lakes that are at risk of mercury pollution, given the relation between DOC and mercury concentration. Potentially, this may reduce the amount of sampling that would otherwise be necessary in the field, thereby reducing costs, and may assist in the early diagnosis of a potential human health risk

2.0 Background

2.1 Kejimikujik Project

Figure 2-1 shows the location of Kejimikujik National Park in Nova Scotia.

Research in the park conducted over the past five years has focused on the sources, fate and effects of mercury within the environment because it is located in an acid-sensitive area downwind from major pollution centres in the northeastern US and southeastern Canada (Beauchamp et al., 1998; Burgess et al., 1998a,b; Clair et al., 1998; Boudala et al., 2001). The Meteorological Service of Canada has operated a daily precipitation and air quality monitoring station in the Park since May 1979 (Parks Canada, 1998). Samples are analyzed for acidity and for the concentrations of pollutants, including sulphates, nitrates, ozone and other compounds of concern.

Studies done in the park have indicated that mercury concentrations are causing health effects in some species of wildlife, particularly loons. Burgess et al. (1998a) have shown that loons at Kejimikujik have accumulated mercury in their blood. There are over 30 nesting pairs of common loon within the park and the Kejimikujik population has mercury concentrations in their blood that are more than twice that of any other population studied (Burgess et al., 1998a). This can be seen in Fig. 2-2 and has occurred because loons are positioned at the top of their food chain and are therefore at the top of the mercury biomagnification pyramid. In summary, the mercury in the water is being ingested by phytoplankton. The phytoplankton are then ingested in large numbers by the fish, which are, in turn, eaten by the loons. Mercury accumulation has been affecting

Figure 2-1: Location of Kejimikujik National Park in Nova Scotia (Parks Canada, 1998)

Figure 2-2: Mercury concentrations in loon blood from various regions (Burgess et al., 1998a)

the loons adversely by altering their behavioral patterns and reducing their reproductive success (Burgess et al., 1998b). Although the negative impacts of the mercury are well understood, the exact source of the increased mercury concentrations in this particular part of the province remains uncertain.

2.2 *Possible Sources of Mercury*

The mercury in the natural environment comes from various sources, including natural and anthropogenic sources and the re-emission of current mercury stocks due to its high volatility (Mitra, 1986). Fig. 2-3 shows the fundamental transfers that occur as mercury cycles through the environment. Mercury occurs in the natural state only in small amounts, estimated at 50 to 80 ppb of the earth's content (Friberg and Vostel, 1972). Deposits can be found in all types of igneous, metamorphic and sedimentary rock, but in Kejimikujik mercury is more prevalent in the granite bedrock than in the surrounding slates and quartzites, although very little is known about actual concentrations (Rutherford, 1998). These deposits can be released through natural degassing or chemical weathering of the rocks (Friberg and Vostel, 1972).

Anthropogenic sources have been studied at Kejimikujik through the use of air monitoring stations and collecting information concerning regional mercury emissions. Air pollution generated in the midwestern and eastern United States, as well as central Canada, has a major influence on the air quality in Nova Scotia (Beauchamp et al., 1998). Long-range atmospheric transport has historically been cited as the prevailing cause of the elevated mercury levels in this area.

Figure 2-3: Mercury cycling in the environment

Clair et al. (1998) examined the spatial distribution of mercury levels in lakes in the Atlantic Provinces. If the cause of the pollution was limited to long-range atmospheric transport it would be reasonable to predict a gradient of concentrations to have developed over the area. However, the field evidence showed no such spatial distribution. Not surprisingly, high concentrations were found in industrialized areas attributable to point-source pollution, but there were also high concentrations in remote areas, such as Kejimikujik National Park (Rutherford, 1998). This suggested that anthropogenic sources, specifically long-range atmospheric transport, may not be solely responsible for the elevated levels. The trend in concentration due to atmospheric transfer may exist but other factors, specific to each lake, may be modifying it.

2.3 *Mercury in Aquatic Environments*

Research has been done on mercury concentrations in Kejimikujik lakes (Clair et al., 1998; Boudala et al., 1999). Figure 2-4 is an illustration of dominant transformation and transport pathways by which mercury in an aquatic ecosystem moves between the atmosphere, water, sediments, and biota (Gill, 2001). Mercury's chemistry in aquatic systems is complex because a thermodynamically predictable interaction does not exist between solution complexes of inorganic Hg (II) and organo-Hg compounds, such as monomethylmercury, CH₃Hg(II) (Gill, 2001). Monomethylmercury in natural waters and sediments is principally produced by bacteria from inorganic Hg that is naturally present in the ecosystem and from Hg that is added from exogenous sources (Mitra, 1986). The partitioning of Hg between these two pools is kinetically controlled by the net effect of the production (methylation) and destruction (de-methylation) of

Figure 2-4: Dominant transformation and transport pathways by which mercury in an aquatic ecosystem moves between the atmosphere, water, sediments, and biota (Gill, 2001)

monomethylmercury by biologically mediated processes (Gill, 2001). The relative abundance of methylated Hg species in aquatic systems is of particular concern since these compounds are highly toxic and they are the major forms of Hg passed up the food chain.

Mercury scavenging onto particles and particle settling to the sediments is a process that removes mercury from the water column (Gill, 2001). Mercury removed to the sediments can be buried as insoluble mercury sulfides or transformed by bacteria to dissolved monomethylmercury (Gill, 2001). Monomethylmercury can then enter the water column from sediments, where it is incorporated into phytoplankton during growth (Mitra, 1986). Once in the food chain, the concentration of mercury in aquatic organisms increases as larger organisms consume smaller ones.

A portion of the dissolved inorganic mercury pool, Hg(II) , in the water column is also methylated and/or reduced to volatile elemental mercury, Hg(0) , which then degasses to the atmosphere (Gill, 2001). This latter process can occur through the formation of photoactive organic complexes of mercury. Atmospheric mercury is oxidized, then returns to the water surface in rain.

The high concentrations of mercury found in some lakes in Kejimikujik National Park may be due to the mercury becoming complexed with DOC. The amount of complexation that occurs is largely dependent on the unique characteristics of the lake, such as its depth, temperature, surface area, and chemical composition (Boudala et al., 1999). When mercury is complexed to DOC it is more likely to be kept within the lake basin than if it were in free ionic form (Clair et al., 2000). DOC also affects mercury concentrations by shifting the balance between evasion and methylation of mercury. The

presence of DOC favours methylation over evasion, which results in increased residence time of mercury in the water column (Watras et al., 1995).

A trend between levels of mercury and dissolved organic matter has been noticed in lakes at Kejimikujik and other areas of the world. Studies by Clair et al. (1998) in Kejimikujik indicated that natural organic carbon is a strong determinant of the presence or absence of total mercury ($r^2 = 0.69$). This trend was also noted by Boudala et al. (1999) in their study of Kejimikujik lakes. In northern Wisconsin, Watras et al. (1995) found that total mercury concentrations were positively correlated to DOC concentration ($r^2 = 0.83$). Driscoll et al. (1995) found a similar relation in Adirondack Lakes ($r^2 = 0.79$). This relation provides a possible method for the early identification of lakes at risk of mercury pollution by using DOC concentrations as a surrogate for mercury concentrations.

2.4 *DOC and the Optical Properties of Water*

The organic carbon in lakes is a mixture of plant and animal products in various stages of decomposition. The total pool of this material within a water body is made up of dissolved organic carbon and dead particulate organic matter. High concentrations are often found in marshes, lakes and rivers with lower concentrations in estuaries and coastal regions.

The colour of water is the result of a combination of absorption and scattering of light within the water column. DOC absorbs light across through the ultraviolet (280-400 nm) and visible (400-700 nm) portions of the electromagnetic spectrum that might otherwise have been back-scattered by other optically-active components, thereby reducing the potential for reflectance (Witte et al., 1982). Also, DOC itself produces no

significant scattering, therefore its presence does not increase overall reflectance from the lake water. Figure 2-5 shows how absorption of light changes with increasing DOC concentrations. The curves in the figure are theoretical and represent increasing amounts of DOC. Curve A (bottom) has the lowest DOC concentrations and curve C (top) the highest. Absorption at all concentrations decreases exponentially with increasing wavelength (Schindler et al., 1992). Even slight increases in the concentration of DOC within the lake (<2 ppm) increase the absorption of blue and green wavelengths within the lake, but cause very little change in the red and near infrared wavelengths (Bukata, 1995). The result is high relative reflectance in both red and yellow wavelengths leaving the water appearing dark brown (Wetzel, 1983). This phenomenon is prevalent in the lake waters of Kejimikujik and the difference in water colour between clear and dark water lakes is distinguishable by the naked eye.

2.5 *Interference by other Optically Active Components*

Other optically active components, such as chlorophyll and suspended sediments, can also influence the volume reflectance of natural waters (Bukata et al., 1995). Chlorophyll is typically the main constituent responsible for variation in the reflectance spectrum of water (Arenz et al., 1996). Figure 2-6 depicts three typical absorbance spectra for various types of phytoplankton. Absorption is greatest in the blue region of the spectrum, with a significant peak in the orange to red region of the spectrum. Absorption is the lowest in the green region, hence the green colour of water

Figure 2-5: Effect of DOC on absorption of light within lakes in the visible portion of the electromagnetic spectrum (SERC, 2001). Theoretical curves A, B, and C represent increasing concentrations of DOC with A having the lowest concentration and C the highest.

Figure 2-6: Effect of three types of chlorophyll on the absorption of light within lakes (SERC, 2001).

associated with high concentrations of chlorophyll. The presence of chlorophyll in waters often interferes with the identification of DOC concentrations as the signals tend to overlap and the chlorophyll signal overpowers the DOC signal (Bukata, 1995).

Suspended sediment, both organic and inorganic in origin, scatters radiation strongly. In moderate to high concentrations this backscattering can overwhelm the reflectance signal caused by chlorophyll or DOC and make detection problematic (Lathrop, 1992).

Estimation of one optically-active component in the presence of varying concentrations of other components that also affect inherent optical properties and therefore reflectance, makes remote quantification difficult (Vertucci and Likens, 1989).

2.6 *Relation between DOC and Landcover*

Nearly all of the organic matter in a lake comes from plants; less than 10% comes from animals (Wetzel, 1983). A high proportion of this comes from terrestrial sources in the surrounding watershed (Wetzel, 1983). Foliage from trees and ground vegetation can provide significant inputs of organic matter into the lakes, and the amount is dependent upon the plant species (Wetzel, 1983). Studies conducted by Hongve (1999) show that fresh litter on the forest floor releases more DOC than older litter. The needles and other products of coniferous origin are decomposed mainly by fungi, which degrade primarily humic acids. Replacement of coniferous needles occurs on a continuous basis and so the DOC released from this source is relatively constant throughout the year (Hongve, 1999). Litter of deciduous vegetation is decomposed more readily by both fungi and bacteria to primarily fulvic acids (Wetzel, 1983). Deciduous trees lose their leaves in the fall season, providing a large source of new leaf litter on the forest floor. This fresh litter, during a

wet period of the year, rapidly releases DOC and can account for the seasonality that has often been observed with regards to DOC concentrations in lakes (Hongve, 1999). Overall, coniferous forests produce higher amounts of DOC than do deciduous forests, but the composition of the DOC is such that it contains more labile components and so is biodegraded more quickly (D'Arcy and Carignan, 1997; Khomotova et al., 2000). The distribution of these trees within the watershed may have an affect on the potential DOC concentration of the lake in question.

Wetlands exhibit high rates of microbial degradation, which can generate massive amounts of organic matter (10-100 times more than upland areas), which is transported to lakes, primarily in the dissolved form, via surface water flow and groundwater flow (Gergel et al., 1999). As a general rule, the wetter the soil the more organic matter is transported to lakes (Mann and Wetzel, 1995). Wetlands are saturated areas that often hold a large amount of organic matter that has been carried in by wind, litter fall or streams. As this organic matter remains in the water it is decomposed by bacteria and fungi and the amount of DOC in the water increases (Wetzel, 1983). This water eventually flows from the wetlands into lakes causing significant increases in DOC, up to twice the original amount (Wetzel, 1983).

Human developments within the watershed of the lake can also affect the DOC concentration. Depending on the type of development the DOC can either be increased or decreased. Clear-cut forestry in a portion of the watershed would cause an initial increase in the amount of organic matter traveling into streams and lakes from leaf litter and disturbances to the forest floor. Conversion of this area into fields for campgrounds would result in further change to the amount and type of organic matter available to the

lake or stream. As the majority of DOC in most lakes originates from terrestrial sources, alterations in the landcover or land use could affect the total concentration of DOC in the lake. France et al. (2000) studied 116 boreal lakes and the impacts of land use modifications. They found that DOC increased in relation to the severity of forest clearance that had been conducted in the previous 4-13 years. Specifically, DOC concentrations in lakes located within clearcut or burnt watersheds averaged 2-3 ppm higher than DOC in lakes located in undisturbed watersheds.

2.7 *Landsat Thematic Mapper Satellite Imagery*

Landsat TM imagery was chosen for use with this project for a number of reasons. Due to the relatively large image size of Landsat, the entire area of Kejimikujik National Park can easily be contained within one frame. This helps to minimize errors associated with the matching of image frames. Another benefit of Landsat images is the ability to conduct temporal studies. Any area on the earth can be imaged once every fourteen days. This facilitates temporal studies of the park and allows comparison of DOC concentrations between seasons and years.

There are also some disadvantages associated with the use of Landsat imagery, the most important being that Landsat is not capable of acquiring images of the earth surface in the presence of clouds or haze in the atmosphere. If clouds are present over the area during the time of acquisition, large areas of the image can be unusable. This unusable area is also extended to areas that are located under the shadow of the cloud, where the reduction of incoming solar radiation alters the amount of radiation returning

to the sensor. This often limits the number of images available for use, especially in areas where cloud cover is a common occurrence, such as Nova Scotia.

Atmospheric haze is also a problem associated with Landsat imagery. Haze causes scattering and absorption of the signal as it passes from the Sun to the Earth's surface and back to the sensor (Lillesand and Kiefer, 1987). Atmospheric correction of the imagery can help to reduce this problem, but can only be truly successful when incorporating atmospheric properties measured during the time of image acquisition (Chavez, 1989). A weather station located within Kejimikujik measures the optical path length, which was incorporated into the 6S atmospheric correction that was used for this Landsat image. The benefit of removing the atmospheric effects is that it allows the image to be compared to other Landsat images acquired at different times. Unfortunately, as the correction is not completely accurate there may be some inherent loss of information (Chavez, 1989).

3.0 Methods

3.1 Study Area

Kejimikujik National Park is located on the Southern Upland of Nova Scotia. The area has little topographic variation and lacks major escarpments, mountains and valleys that are common in other parts of the province. The last glaciation, which started 100,000 to 80,000 years ago, was responsible for shaping many of the landforms present throughout the park. These include numerous drumlins, shallow lakes connected by wandering streams, and granite boulders. The glacial action was highly influenced by the underlying bedrock and so most of the landforms occur in areas of slate, which were easily eroded.

Slates and quartzites dominate the geology of the area (Parks Canada, 1998). However, the southwestern portion of the park is influenced by a massive intrusion of granite, which extends in an arc from Yarmouth to Halifax and outcrops over an area of 10,000 km² (Frey, 1966). The physiographic effects of this intrusion are associated with its hydraulic conductivity/permeability. Water can penetrate the body of granite only along joints or fractures, which may be several metres apart (Parks Canada, 1998). Most precipitation is therefore held on the irregular surface in numerous interconnected bogs, shallow lakes and streams.

Eighty percent of Kejimikujik is considered backcountry to which access is limited. The forest in these areas is representative of the Atlantic Uplands forest region, including mixed coniferous and deciduous vegetation. There is a mixture of tree species but the dominant trees include white pine (*Pinus strobus*), eastern hemlock (*Tsuga canadensis*), white birch (*Betula papyrifera*) and red maple (*Acer rubrum*). The average

age of the forests within Kejimikujik National Park is less than 100 years as a result of fires and logging, but there are some groves of towering eastern hemlock over 300 years old within the park.

3.2 Lake Selection

There are a total of thirty-one lakes located within Kejimikujik National Park. Data on many of these lakes have been collected in previous years for other studies. In 1997 a survey of fifty lakes in and around the park was completed via helicopter, to measure a number of variables involving lake chemistry and hydrology. On-site measurements included pH, dissolved oxygen content, and water temperature. Samples were also collected for the determination of concentrations of total carbon, DOC, total mercury and mercury in sediments. Flushing rates were also computed for each of the lakes. The flushing rate is the number of times per year that the volume of a lake drains and is computed using the volume of the lake and the discharge rate measured at the lake outflow points. The flushing rate for these lakes was reported by Ehrman et al. (1993).

Lakes were chosen for sampling in this project based on these previously-collected data. The selection was limited to a group of twenty-four lakes located within the park boundaries to facilitate sampling. Six variables were chosen for use that were considered to be the most important for this study as they were related to DOC and mercury concentrations. The variables chosen were total carbon concentration, DOC concentration, total mercury concentration, the concentration of mercury in sediments, pH and flushing rate. These data were examined and lakes were then selected to provide a wide range in values in all of the variables. For example, for the variable total carbon

concentration, a lake was chosen to represent each of the percentile classes (100-90, 90-80, 80-70, 70-50 and 50-0), resulting in the selection of five different lakes. This was repeated for each of the six variables, with some lakes fulfilling criteria for multiple variables. When a choice of lakes with similar characteristics was available, lakes were selected to obtain a wide spatial distribution throughout the park, to minimize local effects of geology or landcover. The data available for selected lakes are given in Table 3-1, which shows the physical and chemical properties of water from lakes studied in Kejimikujik. This process was believed to provide the best possible method to ensure a thorough coverage of hydrological variations throughout the park.

As previously stated, eighty percent of Kejimikujik National Park is backcountry to which access is limited. There is one road that traverses the southern portion of the park, providing direct access (minimal portages) to fourteen lakes and indirect access (significant portages) to three more lakes. A road to the northern portion of the park provides access to only two lakes. The remainder of the lakes within the park were inaccessible by vehicle and required hiking significant distances, which was impractical with all of the required equipment. These lakes were removed from the study and so the spatial distribution of the lakes was limited to the southern portion of the park with two additional lakes in the northeastern corner. Time constraints also placed a limitation on the number of lakes that could be sampled and so the previous selection of lakes was prioritized to assure that a wide range in values was covered for each of the previously-defined variables. Spectral sampling of the lake water required taking a boat with equipment onto the lake for a period of time. Accessibility and time constraints limited the number of lakes available for spectral sampling to thirteen.

Table 3-1: Physical and chemical properties of water from selected lakes in Kejimikujik National Park

Lake Name	Flushing Rate (times/year)	Hg in Water (ppt)	Hg in Sediments (ppt)	Total Carbon (ppm)	DOC (ppm)	pH
Back	2.0	2.44	0.13	3.6	3.03	5.46
Beaverskin	1.0	1.54	0.05	2.1	2.18	5.23
Big Dam East	1.6	2.78	0.11	2.9	2.89	5.82
Big Dam West	13.1	5.01	0.06	8.0	5.60	5.20
Big Red	9.6	7.40	0.12	14.1	13.14	4.17
Cobrielle	3.8	2.60	0.09	2.2	2.02	5.34
George	319.0	4.19	0.09	7.6	4.39	5.21
Hilchemakaar	1.7	3.18	0.09	4.3	2.89	5.37
Loon	418.0	3.87	0.14	7.1	3.86	4.57
Lower Silver	3.0	1.53	0.07	3.4	2.66	5.20
Luxton	2.8	4.54	0.14	5.5	2.89	5.08
North Cranberry	6.1	1.93	0.08	5.9	3.55	4.86
Pebbleloggitch	2.9	4.75	0.19	6.2	3.71	4.57
Peskawa	4.6	3.80	0.13	N/A	2.85	5.26
Peskowesk	2.7	2.74	0.19	2.6	3.27	5.94
Puzzle	2.0	.87	0.08	7.4	4.72	5.15
Upper Silver	1.4	1.83	0.05	6.8	4.09	4.64

Water samples were usually taken simultaneously with spectral samples, but could also be collected from the shoreline of the lake, as the concentration of DOC throughout the lake remains relatively constant (Arenz et al., 1996). To maximize the number of samples available for analysis, water was collected from a larger number of lakes ($n = 18$). The locations of the lakes chosen for sampling are shown in Fig. 3-1 with the sampling sites shown in Fig. 3-2. A global positioning system (GPS) was used to record the location of each sampling site. Table 3-2 gives the depth of water at the point of sampling and the type of sample collected at each site.

3.3 *Water Samples*

Water samples were collected from a total of eighteen lakes within Kejimikujik National Park and analyzed for DOC concentration and total mercury concentration. Samples were collected within the uppermost 30 cm of water and sample bottles were capped below the water surface to avoid collecting floating organic matter such as pollen. Samples were collected in 1 l high density polyethylene (HDPE) bottles, which were chosen to minimize contamination of the sample from the bottle surface. As a further precaution the bottle was rinsed three times with lake water before the sample was collected to remove any possible contaminants. After collection the samples were filtered using a 0.45 μm millipore syringe filter to remove particulate matter. The DOC samples were stored in 50 ml centrifuge tubes.

The total mercury samples were stored in 50 ml HDPE bottles and treated with 1 ml of bromine chloride to oxidize the mercury in the sample. This converts all forms of

Table 3-2: Location of sampling sites in August 2000

Date	Lake Name	Depth of water at point of sampling (feet)	Water Samples	Spectral Samples
Aug-16	Ben	< 1	X	
Aug-16	Loon	< 1	X	
Aug-16	Luxton	< 1	X	
Aug-18	Back	17.1	X	X
Aug-18	Hilchemakaar	8.2	X	X
Aug-18	Lower Silver	13.4	X	X
Aug-18	North Cranberry	8.2	X	X
Aug-18	Puzzle	8	X	X
Aug-18	Upper Silver	< 1	X	
Aug-20	Beaverskin	< 1	X	
Aug-20	Big Red	4.6	X	X
Aug-20	Pebbleloggitch	4.4	X	X
Aug-20	Peskawa	6.9	X	X
Aug-21	Cobrielle	12.9	X	X
Aug-21	Peskowesk	7.8	X	X
Aug-22	Big Dam East	9.9	X	X
Aug-22	Big Dam West	12.1	X	X
Aug-22	George	5.5	X	X

the mercury into Hg^{2+} so that it does not precipitate or volatilize out of solution before analysis is conducted. The bromium chloride also breaks down all organic matter in the sample to free the mercury that was complexed to the organic matter. All of the samples were stored in the dark and on ice until laboratory analysis to prevent bacterial growth and the transformation of DOC via photoreduction.

The DOC samples were analysed using the Shimadzu method, a colourimetric method with a detection level of 1 ppm DOC. The total mercury samples were analysed using a Tekran 2537A mercury vapour analyzer as described in Hall and Pelchat (1999). The detection limit of this method is 0.8 ppt mercury and instrumental precision is typically one percent of the relative standard deviation for levels of mercury ranging from 10 to 200 ppt.

3.4 Spectral Measurements

Spectral measurements were taken simultaneously with the water samples in a total of 13 lakes (Table 3-2). The measurements were taken using a SE590 field portable spectroradiometer. This device consists of a data analyzer/data logger, which was attached to a laptop computer. The laptop allowed for immediate access to the data so that any problems could be identified and corrected on site. The data analyzer processed the signal from the spectral detector head and then amplified and digitized it with 12-bit resolution. For each scan the controller activated the shutter. It then measured and stored the dark current, calculated optimum integration time, acquired the spectrum and automatically subtracted the noise for all 256 spectral elements. The spectral range of this device was 370 to 1132 nm, but the working range was limited to 370 to 900 nm. At

wavelengths greater than 900 nm the signal was contaminated by noise from lower wavelengths and so the resulting spectral curve displayed higher reflectance values above 900 nm than were actually present.

The data logger was attached to two sensor heads to allow for measurement of incoming and outgoing radiation. The spectral detector heads use a defraction grating as the dispersive element and the spectrum is imaged onto a 256 element photodiode array. Each element integrates simultaneously, acquiring the spectrum in a fraction of a second. The heads have a standard acceptance angle of 6 degrees. Figure 3-3 shows the internal components of the detector heads used with the field spectroradiometer. The heads have the same spectral range but measure reflectance at different wavelengths. Head 1400 looked upwards and measured solar radiation at the time of sampling. The second head (1283) looked downwards and measured reflectance from the lake water. This head was held approximately 50 cm above the water surface and 50 cm from the side of the boat. In each lake the sensor heads were placed on the sunlit side of the boat to avoid measuring the spectral reflectance within the shadow of the boat, which would reduce the overall value. During measurements two anchors were used to prevent the boat from drifting or rotating. This was important, due to the variable nature of the lake bottom and to keep the sensor on the sunlit side of the boat. The analyzer was set up so that each time the operator requested a scan it would automatically complete a total of four scans and then compute and report the average of those. This was to minimize the alterations in reflectance that are caused by waves on the surface of the lake. Ideally, sampling would only have occurred on days with little wind and sunny, cloud-free skies. Time constraints

Figure 3-3: Internal components of the spectral detector heads used with the SE 590 field spectroradiometer

during the field period meant that sampling had to occur on days with a few clouds and light to moderate winds. To reduce the error that was introduced by these weather conditions a total of ten scans were completed at each site.

Samples were only taken where the lake bottom was not visible to the operator. This was done to minimize the impact of light interactions with the lake bottom on the measured reflectance values. Lake bottoms can be composed of various materials, such as rock boulders or unconsolidated sediments. Rocks have a light coloured surface and a much higher reflectance than the dark coloured sediments. This variation would have introduced an additional complication, interfering with the DOC signal when trying to measure the reflectance caused by the lake water. By ensuring that the lake bottom was not visible, this interference was minimized if not completely eliminated. This required that sampling was in areas of different depths depending upon the clarity of the lake water. In clear-water lakes the bottom was visible to depths of six feet and so sampling was only done at depths greater than seven feet; in dark water lakes, the bottom was only visible to two feet and so measurements were taken at depths of three feet or more. The depths of the collected samples are shown in Table 3-2.

3.5 Calibration of Spectroradiometer

Prior to use in the field the spectroradiometer was calibrated using a light source with known radiance properties. The spectroradiometer was used to measure the radiance resulting from this light source. The known radiance divided by the measured signal provides a measure of the responsivity of the sensor as shown below in equation 3-1.

$$\frac{\text{Signal (counts)}}{\text{Radiance } (\mu\text{W}/\text{cm}^2/\text{nm}/\text{steradian})} = \text{Responsivity (counts}/[\mu\text{W}/\text{cm}^2/\text{nm}/\text{steradian}]) \quad [\text{Eq. 3-1}]$$

The responsivity values were calculated for each wavelength. Responsivity values were used to calibrate field measurements by rearranging the equation, with the responsivity becoming the known value and the radiance being computed as shown in equation 3-2.

$$\frac{\text{Signal (counts)}}{\text{Responsivity (counts}/[\mu\text{W}/\text{cm}^2/\text{nm}/\text{steradian}])} = \text{Radiance } (\mu\text{W}/\text{cm}^2/\text{nm}/\text{steradian}) \quad [\text{Eq. 3-2}]$$

The data provided by the spectroradiometer are given as delimited text. These data must be transposed and columnized prior to calibration. The calibration is then conducted to compute radiance values from the raw data. The next step is to create a ratio of water radiance divided by sky radiance to normalize each of the lakes for the amount of incoming radiation at the time of sampling. As previously stated, the sensor heads measure at different wavelengths. This must be corrected to allow the computation of this ratio.

To correct this, the data from the sensor head measuring incoming radiation (sky) were spread out and four data points were interpolated between each set of original data points. The data were then resampled so that the wavelengths from the sky sensor match those generated from the water sensor. This is done using linear interpolation in the formula given in equation 3-3, where x' is a wavelength from the water sensor head.

$$y' = [(y_2 - y_1)(x' - x_1)/(x_2 - x_1)] + y_1 \quad [\text{Eq. 3-3}]$$

This step generated wavelengths and radiance values for the incoming radiation that could easily be compared to those for the outgoing radiation. The ratio of water radiance divided by sky radiance was then computed and plotted on graphs. This created a spectral plot for each lake. Wavelength in nm was plotted on the x-axis and the ratio (radiance/radiance) was plotted on the y-axis.

3.6 *Analysis of outliers*

Ten spectral curves were recorded for each lake whenever possible. Fewer than ten curves were measured at some lakes due to equipment problems that were recognized only after field work had been completed. Only six curves were recorded for Big Red Lake because the weather deteriorated while sampling on the lake.

After plotting all of the spectral curves for each lake, outliers were identified. Outliers were defined as curves that exhibited differences in either pattern or amplitude from the majority of curves. Once the outliers were identified they were removed from the analysis and not included in the calculation of the median reflectance curve.

An additional problem was identified when comparing the curves of all of the lakes together. Big Red and Lower Silver lakes were identified as outliers that were caused by overcast skies and equipment problems, respectively. At this stage these two lakes were removed from the study, reducing the number of lakes with spectral information to eleven.

3.7 *Correlation and Regression Analysis of Spectroradiometer Measurements*

Once the outliers were identified and removed from further analysis the remaining curves were then used to compute the median. The median was chosen as a measure of central tendency rather than the mean because it is more robust and less subjective to extreme values (Tabachnick and Fidell, 1996). The median spectral curves for eleven lakes were then utilized in the regression analysis. Descriptive statistics were examined for all of the eleven spectral curves and for DOC concentrations. The variables were all logarithmically transformed to improve Gaussian normality.

The first step of the regression analysis was to identify which wavelengths were highly correlated with the dependent variable (DOC). For all 11 lakes the reflectance at each wavelength was regressed against the concentration of DOC. The r^2 value and the significance level were used to determine the extent of correlation and significance between the variables. Once the significantly-correlated wavelengths were identified, a selection of nine wavelengths was chosen for further analysis.

At this stage the impact of chlorophyll was considered. Various authors have suggested that wavelengths that are representative of chlorophyll absorption features can help to normalize the resulting equation for the concentration of chlorophyll in the water (Vertucci and Likens, 1989; Arenz et al., 1996). For these purposes five wavelengths were chosen because they are wavelengths that are significantly affected by the presence of chlorophyll. Peaks of absorption for chlorophyll occur at 445 and 665 nm and the minima of absorption for chlorophyll occur at 520 and 550 nm. The fifth wavelength chosen, 700 nm, is the wavelength exhibiting the maximum spectral shift associated with the presence of chlorophyll (Arenz et al., 1996).

The presence of DOC in the lakes was accounted for by including four additional wavelengths. These wavelengths were chosen because they were the wavelengths from the initial regressions that exhibited the highest correlation and therefore the highest r^2 values in each of their spectral regions. Reflectance in the ultraviolet region of the spectrum was represented by 395.5 nm, blue by 454.2 nm, green by 576.3 nm and red by 601.8 nm. It has been shown that ratios of wavelengths can produce higher r^2 values than single wavelengths (Arenz et al., 1996). These nine wavelengths were then combined into all possible ratio combinations ($n = 72$) and regressed against DOC concentration to identify which ratios had the highest predictive power.

Multiple regression models, those that include multiple variables, often have higher predictive power than linear regression models because they explain more of the variance in the dependent variable by including more independent variables (Tabachnick and Fidell, 1996). The ten ratios with the highest r^2 values were entered into a multiple regression equation as the first independent variable, in a model in which the second independent variable consisted of a ratio that exhibited two characteristics: (1) it had the same reflectance denominator as the initial ratio and (2) the numerators consisted of reflectance at each wavelength across the spectrum. Each possible combination of variables ($n = 1810$) was then regressed against DOC to create multiple regression models. The final models were compared with those created in other studies to assess the compatibility of the models and the utility of applying the model to another study area.

3.8 Acquisition and Processing of Landsat TM Image

Ideally, a satellite image acquired in August 2000 would have been used for analysis, to ensure that the satellite data were related to the field measurements. The satellite image available for this date exhibited cloudy sky conditions and the spectral information for many lakes was not accessible.

As an alternative to the reduction of sample size, a Landsat image acquired on September 13, 1999 was used. The portion of the image containing Kejimikujik is cloud free and so allows sampling of all eighteen lakes. The Landsat measures reflectance in six bands and emittance in one band but for the purposes of this study only bands one through five and seven were used. The description of these bands is given in Table 3-3.

DOC concentrations within the lake can vary both seasonally and annually (Wetzel, 1983). Seasonal changes can be substantial and often correspond to growth and senescence of vegetation within the watershed (Gorham et al., 1998). Annual changes in the concentration of DOC in the lakes are generally smaller and relative changes occur between all lakes in the area (Wetzel, 1983). These changes are a possible source of error for this analysis due to the use of a satellite image that was not acquired at the same time as water samples.

Remote sensing from satellite platforms of land or water surfaces in the visible and near infrared is strongly affected by the nature of the atmosphere along the path from sun to target (surface) and back to the sensor. Before conducting any analyses using this Landsat image, the first step must be to attempt to correct the image for atmospheric effects. The atmosphere affects images through the scattering, absorption and refraction of light, but the most prevalent of these is usually scattering, especially in the visible

Table 3-3: Spectral range and description of the six bands of Landsat Thematic Mapper

Band	Spectral Range (nm)	Description
TM 1	450 – 520	visible blue – green
TM 2	520 – 600	visible green
TM 3	630 – 690	visible red
TM 4	760 – 900	near infrared
TM 5	1550 – 1750	infrared
TM 7	2080 – 2350	infrared

region of the spectrum (Chavez, 1989). These effects are both additive (scattering) and multiplicative (absorption), and various methods have been developed for their correction.

The method used for this image was 6S (Second Simulation of the Satellite Signal). This is a computer code developed in 1995, which can accurately simulate the above problems, thereby correcting the imagery for the effect of the atmosphere and bidirectional reflectance (Vermote et al., 1997). The complete manual for 6S is available from anonymous ftp on kratmos.gsfc.nasa.gov (128.183.112.125). The correction of the imagery was completed using the optical path length measured at the Kejimikujik weather station at the time of acquisition (P.White, personal communication, 2000). Other inputs to this procedure can be altered to produce the best results for the time of acquisition and the atmospheric conditions at that time.

This correction resulted in the conversion of digital numbers from the raw image to reflectance data, which can be used for temporal studies. The correction had some unfortunate impacts on the imagery that caused the first band to have reflectance values equal to zero. The high scattering present in the blue portion of the spectrum probably caused this problem. Although reflectance data were preferred for this study, it was also important to retain the information present in the first band of the imagery. To alleviate this problem both raw data and the corrected reflectance data were used in the required analyses.

3.9 *Sampling of Lake Reflectance from Landsat TM Imagery*

The goal of sampling the lake reflectance data was to use these values to predict DOC through the development of a regression model. To facilitate this, the reflectance values of the lake water were sampled in the same eighteen lakes as water sampling in the field. For each of the eighteen lakes a point was selected that was toward the centre of the lake and away from all edges or islands. This was to ensure that a sample of twenty-five pixels could be taken from each lake without including edge pixels affected by the adjacency effect. The adjacency effect is caused by the scattering of light that is travelling from the surface of the earth back to the satellite sensor. Depending upon the landcover type along the shoreline of the lake, scattered light could make the lake water nearby appear to be lighter or darker than it actually is. This effect is not corrected during the atmospheric correction and so is present in both the raw data and the radiance data. To avoid these effects, pixels near the edge of the lake were not included in the analysis. A second reason for excluding these pixels is bottom reflectance. When the water is very shallow, such as in near-shore areas, light penetrates to the bottom of the lake. When this happens, the interaction of the light with the lake bottom alters the reflected values and the results can no longer be attributed solely to the water chemistry.

Once an appropriate site was selected in each lake, a sample of twenty-five pixels was recorded. This was done for each of the Landsat TM bands 1 through 5, for both the raw data and the radiance data. The average value for each of the bands was calculated and used for further analysis.

3.10 *Statistical Analysis of Landsat TM Lake Reflectance*

Prior to beginning any statistical tests, the normality of the variables was tested. A list of the variables used and their descriptive statistics are given in Table 3-4. DOC was the only variable that was skewed and so a log transformation was performed on this variable to improve its normality. A correlation matrix was constructed to analyze the correlation that existed between all of the variables and to identify which bands explained most of the variation in DOC. Once this was completed the variables were regressed against DOC using two methods. The first was to enter all of the variables into the regression at the same time (forced entry method). This method allowed the creation of a model for the prediction of DOC that included all variables for which data was collected. The second method was a stepwise regression. This method uses only those variables that explain a significant amount of the variance in DOC and created a second regression model.

A cluster analysis was also completed to assess whether the reflectance data could be used to classify the lakes into empirical (high or low) classes. The purpose of the project is to predict the DOC concentration and identify lakes at risk of mercury pollution. This does not necessarily require an accurate prediction of DOC but rather a precise classification of high or low concentration. The cluster analysis groups lakes whose variables are the most similar, thereby identifying relatively homogeneous groups based on spectral reflectance. This was done to assess whether the lakes exhibited spectral reflectance measurements that were different enough to be classified into separate classes.

Table 3-4: DOC concentrations and spectral reflectance variables used for statistical analyses with their descriptive statistics

	N	Min	Max	Mean	Std. Dev.	Skewness	Std. Error	Kurtosis	Std. Error
RAW DATA									
DOC	18	2.80	13.10	5.52	2.47	1.95	0.53	4.54	1.04
LOG (DOC)	18	0.45	1.12	0.71	0.16	0.89	0.53	1.02	1.04
TM1	18	55.96	60.20	57.64	1.11	0.58	0.53	-0.09	1.04
TM2	18	30.36	33.72	32.12	1.09	0.23	0.53	-1.26	1.04
TM3	18	20.92	23.52	22.07	0.64	0.58	0.53	0.29	1.04
TM4	18	14.00	16.52	15.28	0.66	-0.16	0.53	0.42	1.04
TM5	18	8.60	10.16	9.49	0.37	-0.74	0.53	1.07	1.04
TM7	18	8.40	8.96	8.65	0.16	0.41	0.53	-0.61	1.04
RADIANCE DATA									
DOC	18	2.80	13.10	5.52	2.47	1.95	0.53	4.5431	1.04
LOG (DOC)	18	0.45	1.11	0.71	0.16	0.89	0.53	1.0185	1.04
TM2	18	15.04	19.16	17.02	1.27	0.11	0.53	-1.1281	1.04
TM3	18	36.92	40.96	38.62	1.09	0.46	0.53	-0.4601	1.04
TM4	18	31.44	36.16	33.50	1.54	0.34	0.53	-1.2752	1.04
TM5	18	12.72	14.36	13.64	0.45	-0.35	0.53	-0.1228	1.04

3.11 Classification of Landsat TM Image

A Landsat image acquired on August 10, 1999 was classified into seven landcover classes (A. Rencz, personal communication, 2001). Since Kejimikujik is a national park it is a protected area and although the image was acquired one year prior to this study, the image still offers a good representation of the landcover in Kejimikujik.

This classification was prepared by creating training polygons to allow the computer to recognize each individual landcover type. The training polygons were based on airphotos and a topographic map. The topographic map used was mapsheet 21 A6, which is at a scale of 1:50,000. Airphotos for ground truthing were obtained at a scale of 1:50,000. *A priori* knowledge of the area was also used to help delineate appropriate training polygons. Once this was complete, the image was classified using a maximum likelihood classifier. Maximum likelihood classification (MLC) calculates the probability that each pixel belongs to each class. The pixel is then assigned to the class to which it has the highest probability. The final classification scheme is given in Table 3-5 along with a description of each class.

3.12 Delineation of Watersheds

The next step in the process was to assess what type of landcover surrounded each lake. To do this the watershed of each lake was delineated using the 1:50,000 topographic mapsheet (21 A6) of Kejimikujik National Park. A watershed is defined as the area surrounding a lake from which all precipitation that reaches the ground surface flows into the same lake (Botkin and Keller, 1995). This is determined by topography, therefore the water entering the lake from the watershed can be highly influenced by the

type of landcover that it passes over or through. The watershed of each lake was used as a mask over the landcover classification and the total area of each landcover class within the watershed was computed. The total area of the watershed was also computed using this method. These variables were all entered into the statistical analyses as explained below.

3.13 Statistical Analyses of Landcover Classification

The variables used for the analyses are listed in Table 3-6 along with their descriptive statistics. Total land area (totarea) and flushing rate (flushing) variables were added to the landcover classes included in the analysis. To improve the normality of the variables they were all logarithmically transformed prior to further analyses. A correlation matrix was constructed to identify which had the most influence on the concentration of DOC within the lakes. As with prior analyses, two types of regression were performed. The forced entry method (all variables are entered in a single step) was used to create a model for the prediction of DOC. A large number of the variables exhibited multicollinearity and so a stepwise regression was completed to help identify which variables may be responsible for the DOC concentrations. A factor analysis was also performed to assist in the explanation of cause and effect. The residuals of the stepwise regression and the scores from the factor analysis were mapped to identify any possible spatial trends in the data.

Table 3-5: Classification scheme used for landcover classification

Class	Description
Water1	Clear Water
Water2	Water with a low sediment load
Water3	Water with a high sediment load
Conif	Coniferous forest (needle leaves)
Mixed	Mixed forest
Decid	Deciduous forest (broad leaves)
Open	Open areas including, meadows, bog, wetlands and fields

Table 3-6: Variables used for statistical analyses with their descriptive statistics (all variables are logarithmically transformed; see table 3-5 for a description of the variables)

	N	Min.	Max.	Mean	Std. Dev.	Skewness	Std. Error	Kurtosis	Std. Error
DOC	18	0.45	1.12	0.71	0.16	0.90	0.53	1.02	1.03
FLUSHING	15	0.00	1.12	0.47	0.31	0.67	0.58	0.06	1.12
TOTAREA	18	1.87	3.55	2.55	0.51	0.82	0.53	-0.48	1.03
WATER1	18	1.18	2.78	1.72	0.43	1.11	0.53	1.26	1.03
WATER2	18	0.60	1.80	1.09	0.32	0.62	0.53	-0.23	1.03
WATER3	18	0.35	4.11	1.05	0.83	3.16	0.53	11.65	1.03
CONIF	18	1.39	2.93	2.10	0.52	0.49	0.53	-1.06	1.03
MIXED	18	0.99	3.16	1.94	0.64	0.61	0.53	-0.77	1.03
DECID	18	-0.72	3.03	1.37	1.03	-0.15	0.53	-0.37	1.03
OPEN	18	-9.38	2.38	-5.06	3.14	0.74	0.53	0.21	1.03

4.0 Results and Discussion

4.1 *Water Sampling*

The results of the water sampling conducted in August 2000 are shown in Table 4-1. DOC concentrations ranged from 2.8 ppm (parts per million), in Cobrielle Lake, to 13.1 ppm in Big Red Lake. Mercury concentrations ranged from 1 ppt (parts per trillion) in Puzzle Lake, up to 5.9 ppt in Big Red Lake. Figure 4-1 is a scatterplot of DOC concentrations versus mercury concentrations. A linear trendline has been fitted on this graph to illustrate the direction of the correlation between the variables. The r^2 value is 0.86, indicating a strong positive relation. This result agrees with those found by various authors that studied the correlation between DOC and mercury concentrations (Clair et al., 1998; Boudala et al., 1999; Watras et al., 1995; Driscoll et al., 1995).

Figure 4-2 shows the spatial distribution of DOC concentrations throughout Kejimikujik National Park. This figure illustrates that there is no apparent spatial trend in the DOC concentrations. Lakes located close to each other in the park often exhibit very different concentrations. For example, the concentration of DOC in Big Dam East Lake is 3.6 ppm, while the concentration in Big Dam West Lake is double at 7.6 ppm. This suggests that a local factor is responsible for the concentration of DOC within the lake. Factors that are not local in this area, such as climate or geology, would be expected to affect more than one lake, resulting in a spatial pattern.

4.2 *Spectral Measurements*

Upon examination of the spectral curves it was determined that repeatability should be the main factor used for the identification and removal of outliers. The aim of

Table 4-1: Concentrations of DOC and mercury in lakes in Kejimikujik National Park, measured in August 2000

LAKE	DOC (ppm)	Hg (ppt)
Back Lake	4.4	1.2
Beaver Skin Lake	3.9	1.1
Ben Lake	4.6	1.2
Big Dam East Lake	3.6	1.6
Big Dam West Lake	7.6	4.0
Big Red Lake	13.1	5.9
Cobrielle Lake	2.8	1.4
George Lake	6.4	3.0
Hilchmakaar Lake	5.6	1.6
Loon Lake	6.4	2.1
Lower Silver Lake	4.2	1.1
Luxton Lake	5.8	1.8
North Cranberry Lake	4.6	1.4
Pebblelogitch Lake	9.2	3.1
Peskawa Lake	5.3	2.1
Peskowesk Lake	4.6	2.2
Puzzle Lake	3.5	1.0
Upper Silver Lake	3.7	1.2

Figure 4-1: Scatterplot of measured DOC and mercury concentrations

removing outliers was to attain a group of curves that showed similar amplitudes and patterns of reflectance.

A problem associated with obtaining spectral measurements in Kejimikujik is the conduction of field sampling. Ideally, sampling lakes for spectral properties should be conducted on cloud-free, calm days to minimize errors (Vertucci and Likens, 1989). These conditions were not common during the sampling period in August 2000. Sampling was conducted during less than ideal conditions, including partly cloudy skies and/or slight to moderate winds. Figure 4-3 shows a comparison of the measured spectral curves for two lakes. Spectral measurements at Big Dam East Lake were collected during ideal weather conditions (i.e. clear blue sky). As shown in Fig. 4-3(a) all ten spectral curves are very similar and no outliers are present. Sky conditions during the collection of spectral measurements at Peskawa Lake were not ideal, but rather exhibited partial cloudiness. The ten curves collected are shown in Fig. 4-3(b). Curves 5 to 10 are very similar in both shape and amplitude, but curves 1 to 4 exhibit different properties than the other 6. These outliers were caused by fluctuations in the amount of incoming solar radiation due to cloud cover. This was the primary cause of many of the identified outliers that were removed during analysis.

Figure 4-4 shows the median spectral curves that resulted from spectral sampling of eleven lakes in Kejimikujik National Park. The complete group of spectral curves recorded for each lake is given in Appendix 1. The curves for each lake are unique as they represent the total concentration of a group of variable optically-active components. Although the amplitude of the curves is variable they do share some common spectral features. Reflectance in the blue region of the spectrum is low in all cases. For many

Figure 4-3: Comparison of spectral curves measured under clear (Big Dam East Lake) and partially cloudy (Peskawa Lake) sky conditions in Kejimikujik National Park

Figure 4-4: Median spectral reflectance curves for 11 lakes in Kejimikujik National Park

Figure 4-4: Median spectral reflectance curves for 11 lakes in Kejimikujik National Park (continued)

Figure 4-4: Median spectral reflectance curves for 11 lakes in Kejimikujik National Park (continued)

lakes, there is a small peak that is located at approximately 400 nm. This peak corresponds with a wavelength of minimal chlorophyll absorbance. The reflectance gradually increases, in all cases, to reach an initial large peak. Peaks located at approximately 560 nm are associated with low absorption of light by water and DOC. Higher DOC concentrations lead to increased absorption in this spectral region, which in turn causes a shift of this peak to longer wavelengths.

Figure 4-5 shows a comparison of the location of the initial peak wavelengths for Cobrielle and Pebbleloggitch lakes. Cobrielle Lake has the lowest DOC concentration of any lake within Kejimikujik, whereas Pebbleloggitch Lake has the second highest. This graph illustrates the spectral shift that is caused by increasing DOC concentrations. The peak wavelength for Pebbleloggitch Lake has been shifted towards higher wavelengths moving it away from that of Cobrielle Lake. This verifies that there is a recognizable difference between these two lakes based solely on their spectral reflectance.

Figure 4-6 shows the location of the peak wavelengths for all eleven lakes and allows comparison to DOC concentrations. The general trend of this graph shows that the location of the peak wavelength moves to higher wavelengths as the concentration of DOC increases. At DOC concentrations around 4.5 there is a sharp increase in the peak wavelength. This distinctly divides the lakes into two separate groups. The groups with lower peak wavelengths, ranging from 579.1 to 581.9 nm, also have the lowest DOC concentrations, with a range from 2.8 to 4.4 ppm. The second group has both higher peak wavelengths, ranging from 671.9 to 695.8 nm, and higher DOC concentrations, ranging from 4.6 ppm to 9.2 ppm. Since we are primarily interested in identifying lakes with high

Figure 4-5: Comparison of median spectral curves for Cobrielle (clear) and Pebblelogitch (dark) lakes

Figure 4-6: Comparison of peak wavelength location and DOC concentration for lakes in Kejimikujik National Park

DOC concentration, as they are at risk for mercury pollution, those lakes known to have low DOC can be eliminated. This would help to reduce the amount of field work needed by narrowing the possible selection of lakes.

4.3 *Statistical Analyses of Spectral Measurements*

An initial analysis of correlations between DOC and reflectance at particular wavelengths identified a large number of wavelengths that were highly correlated with DOC concentration. Wavelengths were considered highly correlated if they had correlation coefficients greater than 0.6 and were significant at 0.05 (95% confidence level). There were ninety-three wavelengths that exhibited these characteristics. These included all consecutive wavelengths between 388 and 625 nm, as well as those between 708 and 717 nm. Correlation coefficients for these wavelengths ranged from 0.61 to 0.93. This indicates that DOC had a significant impact on the spectral properties of the water at a wide range of wavelengths.

Table 4-2 shows the correlation coefficients for the wavelengths that were chosen for further analysis. The highest correlation ($r=0.93$) occurred at 576.3 nm, which is located in the green region of the spectrum. Five of the wavelengths were chosen because of their relation to chlorophyll. The correlation coefficients for some of these wavelengths, specifically 668.9 and 698.8nm, are low and the correlations are not significant. These wavelengths were chosen because they had been successfully used by other authors (Arenz et al., 1996).

Table 4-2: Pearson product moment correlation coefficients (r) of single wavelengths selected for further analysis

Wavelength	Correlation	Sig. (2-tailed)	Reason for Selection
395.5	-0.801	0.003	Highest correlation in UV
441.2	-0.889	0	Peak absorption by chlorophyll
454.2	-0.903	0	Highest correlation in Blue
520.9	-0.908	0	Minimal absorption by chlorophyll
551.1	-0.908	0	Minimal absorption by chlorophyll
576.3	-0.925	0	Highest correlation in Green
601.8	-0.829	0.002	Highest correlation in Red
668.9	0.170	0.618	Peak absorption by chlorophyll
698.8	0.538	0.088	Maximum spectral shift

A correlation analysis using the ratios of the nine single wavelengths, given in Table 4-2 identified more than sixty ratios that were highly correlated to DOC concentration. The correlation coefficients for these ratios ranged from 0.69 to 0.94. The correlation coefficient, and therefore the predictive power of the regression equation, was increased by using a ratio of two wavelengths ($r^2 = 0.88$) rather than a single wavelength ($r^2 = 0.86$). This correlation was obtained using two different ratios, which are the reciprocal of each other ($698.8 / 668.9$ and $668.9 / 698.8$). It is interesting to note that these were both individual wavelengths that exhibited low, non-significant correlations with DOC concentration. Individually, these wavelengths explained a small portion of the variance in DOC concentration.

Table 4-3 shows the 10 wavelength ratios that have the highest correlations with DOC concentration. These wavelengths were used to create multiple regression equations. The use of multiple wavelength ratios in the formation of a regression equation improved the resulting r^2 value. The r^2 value of the best regression equation was equal to 0.94 and was significant at 0.01 (99% confidence level). Equation 4-1 was the final result.

$$\text{Log (DOC)} = -1.319 - 10.919 (\log [R_{576.3}] / \log [R_{668.9}]) + 13.039 (\log [R_{584.8}] / \log [R_{668.9}])$$

[Eq. 4-1]

The wavelengths in the numerators of the ratios both exhibited high individual correlations with DOC concentration. The denominator of both ratios is the same and is a wavelength of peak chlorophyll absorption. This helps to improve the predictive power of the equation by normalizing it for the concentration of chlorophyll in the lakes.

Table 4-3: Correlation coefficients of single wavelength ratios against DOC which were selected for further analysis

Wavelength Ratio	Correlation	r²	Sig. (2-tailed)
698.8 / 668.9	0.937	0.877	0.000
668.9 / 698.8	0.937	0.877	0.000
601.8 / 698.8	0.919	0.845	0.000
576.3 / 698.8	0.917	0.842	0.000
698.8 / 601.8	0.914	0.834	0.000
551.1 / 698.8	0.912	0.831	0.000
520.9 / 698.8	0.899	0.808	0.000
576.3 / 668.9	0.898	0.807	0.000
698.8 / 576.3	0.897	0.804	0.000
601.8 / 668.9	0.897	0.804	0.000

The residuals of the regression equation, calculated as predicted DOC concentration minus observed DOC concentration, were plotted in Fig. 4-7 to look for spatial trends by examining the distribution of the variables throughout the park. All of the residuals are close to zero, which indicates that this equation is useful for predicting DOC concentrations. There is no distinctive spatial pattern in the residuals, as over predictions and under predictions are spread evenly throughout the park.

Models developed by other authors were tested for their ability to predict DOC concentrations using the data collected in Kejimikujik National Park. The first model tested was developed with reflectance data for Colorado area reservoirs (Arenz et al., 1996) and is given in equation 4-2.

$$\text{DOC} = 0.5 \left([R_{716} / R_{670}]^{-9.60} [R_{706} / R_{670}]^{12.94} \right) \quad [\text{Eq. 4-2}]$$

The wavelength in the denominator is essentially the same wavelength used in the Kejimikujik equation. The numerators are wavelengths that exhibited high single correlations with DOC concentrations in Colorado, but low correlations with DOC in Kejimikujik.

This equation was used to predict DOC for lakes in Kejimikujik with the reflectance data obtained from each lake. A t-test was used to determine if the predictions of the model were sufficiently similar to the measured data to be considered part of the same population. The 2-tailed P statistic for this test was <0.0001, leading to the rejection of the null hypothesis, that there is no statistical difference between the two samples. This suggests that this equation does not provide a successful

method for the prediction of DOC concentrations within the lakes of Kejimikujik National Park.

Arenz et al. (1996) noted that equations developed by authors for other geographical regions did not consistently fit the Colorado data, a fact that they attribute to the varying nature of DOC. DOC that originates from different sources varies with respect to its molecular weight and its composition of humic acids and tannins (Wetzel, 1983). These factors cause the reflectance pattern of the spectral curves to change and can cause a shift of the location of the wavelengths that are correlated with DOC concentration (Arenz et al., 1996).

The second model tested was developed for Adirondack region lakes (Vertucci and Likens, 1989) and is given in equation 4-3.

$$\text{Log (DOC)} = -1.392 (\log [R_{589} / R_{520}]) + 0.685 \quad [\text{Eq. 4-3}]$$

This equation had a r^2 of 0.80 for the prediction of DOC in Adirondack Lakes. The denominator of the wavelength ratio is related to the presence of chlorophyll, but in this case it is a wavelength of minimal absorption. The numerator is very similar to the ones used in the Kejimikujik equation and had a high single correlation with the Kejimikujik data.

The 2-tailed P statistic from a t-test comparing DOC concentrations predicted by this equation to those measured in Kejimikujik was 0.93. This means that the null hypothesis must be accepted since the P value is greater than 0.05, indicating that there is no significant difference between the observed and the predicted values of DOC

concentration. This equation would therefore be useful in predicting DOC concentrations using spectral measures of lakes obtained from Kejimikujik National Park. The ability of this equation to predict DOC concentrations in Kejimikujik is due to the inclusion of wavelengths that are correlated with the data from Kejimikujik Lakes.

Using the equation developed specifically from the Kejimikujik data results is the most accurate prediction of DOC concentrations within the lakes, but equations developed in other geographical regions that include similar wavelengths may also prove to be useful. The high r^2 values indicate that this method of DOC prediction is very successful and proves a useful surrogate for mercury concentrations within the lakes without requiring laboratory analyses of water samples. Unfortunately, this method still requires extensive field sampling.

4.4 *Statistical Analyses of Landsat TM Reflectance Data*

After extracting the spectral information from the Landsat image (both raw and radiance data) the distribution of the data was examined. In both cases the DOC concentration was logarithmically transformed to improve normality. The other variables were already normally distributed and so did not require transformation. Although the raw image data are not useful for temporal studies they were included in this analysis so the utility of bands 1 and 7 for DOC prediction could be further assessed.

Table 4-4 shows the correlation matrix for the raw image data. Only TM1 and TM2 are significantly correlated to DOC concentration at a significance level of 0.05. The correlations of both of the variables with DOC are over 0.80, but negative. This indicates that as DOC increases the spectral reflectance of the lakes decreases in these

Table 4-4: Correlation matrix for raw image Landsat TM data

		LOGDOC	TM1	TM2	TM3	TM4	TM5	TM7
LOGDOC	Correlation Sig. (2-tailed)	1 .						
TM1	Correlation Sig. (2-tailed)	-0.806 0.000	1 .					
TM2	Correlation Sig. (2-tailed)	-0.820 0.000	0.905 0.000	1 .				
TM3	Correlation Sig. (2-tailed)	-0.221 0.378	0.394 0.106	0.406 0.095	1 .			
TM4	Correlation Sig. (2-tailed)	0.336 0.173	-0.229 0.361	-0.059 0.817	0.135 0.592	1 .		
TM5	Correlation Sig. (2-tailed)	0.406 0.095	-0.303 0.221	-0.200 0.426	-0.271 0.277	0.709 0.001	1 .	
TM7	Correlation Sig. (2-tailed)	0.238 0.342	-0.048 0.850	-0.039 0.879	0.094 0.712	0.568 0.014	0.614 0.007	1 .

wavelengths. This was expected because DOC in lake water increases the absorption of light as shown in Fig. 2-4. Some multicollinearity is also evident in Table 4-4. For example, TM1 is highly correlated to TM2 and likewise TM4 is highly correlated to TM5.

Table 4-5 shows the correlation matrix that was constructed for the radiance image data. In this case TM1 and TM7 were not included as variables because of problems with atmospheric correction. The radiance data for these two bands were equal to zero for almost every pixel within the park and so did not add any information to this analysis. TM bands 2,3 and 4 were found to be highly correlated with DOC concentration in the radiance image at a significance level of 0.01. TM5 was the only band that was not correlated with DOC.

The regression analysis was conducted in two steps. The first regression was done using the forced entry method, whereby all variables were entered into the equation simultaneously. The regression equation for the raw image data produced an adjusted r^2 value equal to 0.65, with the standard error of the estimate equal to 0.004 ppm DOC. This equation was significant at 0.01.

Regression using the forced entry method for the radiance data resulted in an equation with an r^2 value equal to 0.61, with the standard error of the estimate equal to 0.101 ppm DOC. This equation was also significant at 0.01 but exhibited less predictive power than the equation using the raw image data. This could be due to the inclusion of fewer variables in the radiance equation.

The second type of analysis was a stepwise regression, which only included variables in the equation if they explained a significant portion of the variability in DOC

Table 4-5: Correlation matrix for radiance image Landsat TM data

		LOGDOC	TM2	TM3	TM4	TM5
LOGDOC	Correlation Sig. (2-tailed)	1 .				
TM2	Correlation Sig. (2-tailed)	-0.819 0.000	1 .			
TM3	Correlation Sig. (2-tailed)	-0.795 0.000	0.943 0.000	1 .		
TM4	Correlation Sig. (2-tailed)	-0.805 0.000	0.993 0.000	0.940 0.000	1 .	
TM5	Correlation Sig. (2-tailed)	-0.425 0.079	0.585 0.011	0.616 0.006	0.564 0.015	1 .

concentrations. The stepwise regression equation for the raw image data included only two variables, TM2 and TM4. These variables alone produced an equation that was significant at 0.01, had an adjusted r^2 value equal to 0.72, with the standard error of the estimate equal to 0.086 ppm DOC. This r^2 value is higher than the one attained using the enter method of regression, which indicates that adding in more variables does not always increase the predictive power of the equation. Equation 4-4 shows the model developed.

$$\text{Log (DOC)} = 3.49 - 0.121 (\text{TM2}) + 0.072 (\text{TM4}) \quad [\text{Eq. 4-4}]$$

This equation used data from bands 2 and 4. Band 2 measures wavelengths between 520 nm and 600 nm. These wavelengths all showed high correlations between ground spectral measures and DOC concentrations. Band 4 measures wavelengths between 760 nm and 900 nm. The utility of these wavelengths for the prediction of DOC may lie in the interaction of DOC and suspended sediments, which is not yet well understood (Arenz et al., 1996).

The stepwise regression conducted for the radiance data also produced better results than the equation developed using the forced entry method, but the equation was not as powerful a predictor of DOC concentrations as the equation developed using the raw image data. This equation had an adjusted r^2 value equal to 0.65, with the standard error of the estimate equal to 0.097 ppm DOC. The equation was significant at 0.01 and used only one variable. The model developed is given in equation 4-5.

$$\text{Log (DOC)} = 2.50 - 0.105 (\text{TM2}) \quad [\text{Eq. 4-5}]$$

This equation used only band 2 and did not incorporate the additional variance explained by band 4 that was included in the equation for the raw image data. Although the corrected data are preferable to the raw data because of the ability for temporal analysis, in this case the predictive ability declines. For future analyses, it may be desirable to attempt alternate methods of atmospheric correction or incorporate more extensive ground measurements of atmospheric properties to improve the correction technique.

A cluster analysis was also conducted on both the raw and the radiance image data. This was to assess whether the lakes were separable based on their spectral information. This analysis groups the lakes that are most alike and using a stepwise procedure eventually groups all of the lakes based on their similarity to each other. Deciding where to stop the clustering procedure was based on the level of dissimilarity that exists between the groups. A large jump in the dissimilarity index occurs when clustering the final two groups of lakes and so the procedure was stopped at this point. Figure 4-8 shows the dendrogram that was produced by the cluster analysis for the raw image data. The lakes are divided into two groups, representing low and high DOC concentrations. The range of DOC concentrations for the high group is 4.55 to 13.1 ppm DOC. The DOC range for the second group is 2.8 to 4.4 ppm DOC. The cluster analysis dendrogram created for the radiance data is shown in Fig. 4-9. This analysis produced the same grouping configuration as that for the raw image data, which shows a consistent ability to separate these lakes based on their spectral properties. It is also interesting to note that this method grouped the lakes in the same configuration as did the peak wavelength analysis shown in Fig. 4-5. This indicates that the spectral measures gathered

Figure 4-9: Cluster dendrogram of four channels of corrected Landsat TM Data from 18 lakes in Kejimikujik National Park using average linkage (between groups)

from the ground and from the satellite have similar capabilities for the prediction of DOC concentrations in the lakes. Both methods accomplish the same task, but the collection of data from the satellite image is much quicker and easier than conducting field studies to collect ground measurements.

4.5 *Statistical Analysis for the Landcover Classification*

A correlation matrix, constructed using the logarithmically transformed variables, is shown in Table 4-6. Only two variables, flushing rate and total area of deciduous forest, were significantly correlated with DOC concentration. There is a considerable amount of multicollinearity present between the landcover variables, which makes interpretation of true correlation with DOC and selection of variables with the most predictive power difficult.

Upon examination of the distribution of the variables, two outliers were identified in the flushing rate variable. George Lake and Loon Lake both had extremely high flushing rates, 319 and 418 times per year respectively. This occurs because they are downstream from Kejimikujik Lake, which has a very large volume that drains through these much smaller lakes; therefore they exhibit characteristics of a river rather than those of a lake. These two outliers were eliminated prior to analysis. Figure 4-10 shows scatterplots of both flushing rate and deciduous forest versus DOC concentrations. Linear trendlines have been added to these graphs to indicate the direction of correlation. Both variables show a wide spread in values but in both cases a statistically significant positive correlation is present.

Table 4-6: Correlation matrix for landcover classes, flushing rate and DOC from Kejimikujik National Park (all variables have been logarithmically transformed; see table 3-5 for variable descriptions)

		DOC	FLUSHING	TOTAREA	WATER1	WATER2	WATER3	CONIF	MIXED	DECID	OPEN
DOC	Correlation Sig. (2-tailed)	1.0000									
FLUSHING	Correlation Sig. (2-tailed)	0.588 0.021	1.000								
TOTAREA	Correlation Sig. (2-tailed)	0.223 0.372	0.422 0.116	1.000							
WATER1	Correlation Sig. (2-tailed)	0.029 0.906	0.253 0.362	0.730 0.000	1.000						
WATER2	Correlation Sig. (2-tailed)	0.110 0.664	0.218 0.434	0.644 0.003	0.936 0.000	1.000					
WATER3	Correlation Sig. (2-tailed)	0.260 0.297	0.580 0.023	0.607 0.007	0.476 0.045	0.336 0.172	1.000				
CONIF	Correlation Sig. (2-tailed)	0.148 0.557	0.351 0.199	0.961 0.000	0.642 0.004	0.569 0.013	0.580 0.011	1.000			
MIXED	Correlation Sig. (2-tailed)	0.311 0.208	0.463 0.081	0.960 0.000	0.631 0.004	0.517 0.027	0.554 0.017	0.893 0.000	1.000		
DECID	Correlation Sig. (2-tailed)	0.535 0.021	0.655 0.008	0.695 0.001	0.477 0.045	0.455 0.057	0.396 0.103	0.549 0.018	0.788 0.000	1.000	
OPEN	Correlation Sig. (2-tailed)	0.187 0.455	0.607 0.016	0.811 0.000	0.541 0.020	0.425 0.078	0.709 0.001	0.698 0.001	0.807 0.000	0.701 0.001	1.000

Figure 4-10: Scatterplots of DOC versus flushing rate and total area of deciduous forest (all variables have been logarithmically transformed)

Regression analysis was again conducted in two steps. The first step was to use all of the variables to create an equation using the enter method. Using all of the variables results in an equation that has an adjusted r^2 equal to 0.74, with the standard error of the estimate equal to 0.089 ppm DOC. This equation is significant at 0.05 but has a very high ratio of variables to cases (9:18), which is problematic (Tabachnick and Fidell, 1996). This method provides high predictive power but does not help the explanation of the cause of variation in DOC concentrations.

To assist with this explanation a stepwise regression was conducted. Due to the low significance levels of many variables the default PIN (probability of F-to-enter) and POUT (probability of F-to-remove) values had to be changed to allow more than one variable to enter the equation. The PIN and POUT were changed to 0.3 and 0.35 respectively, which allowed three variables to enter the equation. These variables were flushing rate, area of deciduous forest and area of open land within the watershed and are shown in equation 4-6.

$$\text{Log (DOC)} = 0.276 + 0.331 (\text{log Flushing}) - 0.029 (\text{log Open}) + 0.084 (\text{log Decid})$$

[Eq. 4-6]

This equation has an adjusted r^2 value equal to 0.41, a standard error of the estimate of 0.135 ppm DOC, and is significant at 0.05. The residuals of this regression (predicted DOC minus observed DOC) were plotted in Fig. 4-11, to identify spatial trends in the distribution of the residuals. A spatial trend could suggest other variables to be included in the equation to increase both the predictive and the explanatory powers of the equation. There is no apparent trend present in this figure, but comparing this

information with that in Table 4-1 indicates that the equation tends to overpredict DOC concentrations for lakes with low concentrations, such as Cobrielle Lake, and underpredict concentrations for lakes with high actual concentrations, such as Big Red Lake. Prediction problems also occurred with George Lake and Loon Lake because the equation includes flushing rate, the values of which are outliers for these two lakes.

Although the stepwise regression equation has lower predictive power than the previous regression equation, it exhibits more explanatory power and indicates that these three variables explain most of the variation in DOC concentrations. For additional verification of the explanatory power of these variables a factor analysis was conducted. The factor analysis divided the variables into two components that explained 83% of the total variance. The first component was composed of a wide mix of variables that related to the total land area of the watersheds and so provided limited explanatory power. The second component was more straightforward and therefore more useful in explanation. The component scores for the second component are shown in Fig. 4-12, which shows that four variables are highly and positively correlated with this component. These variables include the three identified through the regression analysis (flushing rate, deciduous forest and open area) as well as one extra (sediment-laden water). This reinforces the position that these variables are responsible for causing variations in DOC concentrations.

The factor scores for the second component were plotted in Fig. 4-13 to look for trends on the spatial distribution of the scores. No trend is apparent in this figure as the scores are evenly distributed throughout the park. This indicates that this component

Figure 4-12: Factor analysis component scores for the second component from 18 watersheds in Kejimikujik National Park (see table 3-5 for variable descriptions).

probably includes all of the variables required to predict and explain DOC concentrations within Kejimikujik National Park.

Both methods identified three variables as being important in controlling the amount of DOC within the lakes. The first and most important was the flushing rate. It was found that as the flushing rate increased the amount of DOC in the lake also increased. The reason for this correlation is not well understood but could have several possible explanations. The flushing rate of the lake is measured as the number of times per year that the entire volume of the lake is replaced. The flushing rate of the lakes in Kejimikujik is not constant throughout the year (Gorham et al., 1998). High flow occurs during the wet seasons, which in Nova Scotia occur in the spring and fall. During other times of the year flow rates are much lower. At these times water in streams, bogs and wetlands can be stagnant, and the water accumulates high concentrations of DOC. This water is then carried into the lake during storms and periods of higher flow, which causes an injection of DOC into the lake (Gergel et al., 1999). During studies of streams in Nova Scotia, Gorham et al. (1998) found DOC concentrations increased in the stream after periods of drought. Schindler et al. (1992) also found that DOC concentrations in streams were higher after a drought, but showed little relation to flow rates (i.e. remained constant) during wet periods.

Lakes with low flushing rates tend to have low concentrations of DOC. Slow replacement of the lake water introduces little new DOC into the lake. Longer water residence times can lead to increased mineralization of DOC, both biologically and photochemically (Gergel et al., 1999). This causes DOC concentrations to decrease in lakes with longer water residence times (i.e. low flushing rates) especially in lakes with

few wetlands (Schindler et al., 1992; Gergel et al., 1999). Higher flushing rates would replace the DOC more often, therefore causing higher overall DOC concentrations.

Gergel et al. (1999) found that in wetland dominated watersheds the concentration of DOC in streams is inversely related to the flushing rate, due to dilution. According to the landcover classification, the percentage area of wetland within the watersheds of Kejimikujik is less than 10% for each of the lakes. As this is not a wetland dominated watershed we could expect a positive relation between DOC and flushing rate, which was present in this study.

The second predictor of DOC concentration was found to be the area of deciduous forest that is located within the watershed of each lake. Again there is a positive correlation, which indicates that DOC concentrations increase as the area of deciduous forest increases within the watershed. Production and leaching of DOC results in a 25-50% total annual loss of surficial forest floor (Schiff et al., 1997). Deciduous leaves decompose more rapidly than evergreen leaves, which releases DOC to be transported through the soil into the lakes (Chapin, 2001). Deciduous trees also produce more phenolic acids than coniferous trees (Dahlgren and Singer, 2001). These fulvic acids are responsible for the colour of the DOC in the lakes and also provide more complexation sites for mercury and other trace metals.

The third variable found to be responsible for increased DOC concentrations is the area of open land within the watershed of the lake. This variable is an aggregate of a number of smaller land classes that are distributed in small patches throughout the park. These areas include open fields, meadows, bogs and wetlands. D'Arcy and Carignan (1997) found no relationship between DOC concentration and wetland, which they

attributed to the small percentage of wetland area within the watersheds that were studied. The relation in Kejimikujik was also very low ($r = 0.19$), as is the percentage of wetland area within the watersheds ($<5\%$). It is believed that the positive correlation that does exist between this type of area and DOC concentration is caused by the presence of stagnant water. These areas are often saturated by water for most of the year and during this time it attains a high concentration of DOC (Gorham et al., 1998). When this water is flushed into the lake it increases the overall concentration of DOC within the lake.

The presence of this type of land class in Kejimikujik is variable between watersheds but is in general quite low in all cases (i.e. less than 9 Ha). This may be an underestimate due to the use of Landsat imagery for the classification of landcover types. In Maritime climates, there are usually small patches of wetland that are invisible, even in air photos (Gorham et al., 1998). This means that they are also invisible in the Landsat image, resulting in the underestimation of the area of this type of landcover.

Many authors have determined wetland area to be a major factor causing variation in DOC concentration. Driscoll et al. (1995) calculated a r^2 value of 0.85 between DOC concentration and the percent area of wetland located within the drainage basins of the lakes. Watras et al. (1995) found a r^2 of 0.61. Significant, but lower, results were also found by Gergel et al. (1999), Schiff et al. (1998) and Gorham et al. (1998). Schindler et al. (1992) found that per unit area more DOC is exported from wetlands than from upland areas within the watershed. Urban et al. (1989) collected values of DOC export from bogs versus uplands in various parts of North America. Values of export from bogs ranged from $5 - 24 \text{ g m}^{-2} \text{ yr}^{-1}$, while values from upland areas were much lower ranging from $0.5 - 5 \text{ g m}^{-2} \text{ yr}^{-1}$. St. Louis et al. (1994) estimated that rates of DOC and methylmercury

from wetland dominated watersheds are 10-100 times higher than from upland watersheds.

Wetland area is also believed to have an impact on DOC concentrations in Kejimikujik National Park. Although the derived correlation between open area within the watershed and DOC concentration was low it is believed that many wetlands are not visible in the Landsat image. Studies conducted by Gorham et al. (1998) have shown that when wetlands occupy a small proportion of the watershed small increases in that proportion can lead to very pronounced increases in the concentration of DOC, with the relative enhancement decreasing steadily as the proportion of wetlands increases. This indicates that errors in the landcover classification could have a large impact on the derived relation between watershed area and DOC concentration. A better test may be to utilize a classification based on a smaller pixel size from a different remote sensing platform or to utilize a forestry classification created from ground surveys.

5.0 Conclusion

The ability to indicate the potential sensitivity of lakes in Kejimikujik National Park to mercury pollution is the fundamental reason for the completion of this project. Mercury concentrations in lakes are difficult to assess and require sampling in the field and expensive laboratory analyses. For these reasons, scientists doing research at Kejimikujik require a method for the identification of lakes that are sensitive to increased mercury concentrations. This method may be available by studying DOC concentrations in the lakes.

This project identified possible methods for predicting DOC concentrations that limit expensive field work and laboratory analyses. It focused on the use of three procedures for the prediction of DOC – ground spectral measures, satellite spectral measures and landcover classification.

The use of ground spectral measures provided two methods for the identification of DOC concentrations. The first method requires very little analysis and separates the group of lakes into two classes of low and high concentrations based on the location of the peak wavelength. This allows elimination of any lakes classified into the low class, as they are not at risk for mercury pollution, which reduces the number of lakes that require further analysis. The second method uses the spectral data to create a regression equation, with an r^2 equal to 0.94. This indicates that this method is very successful at accurately predicting DOC concentrations. A disadvantage to the use of ground spectral measures is that the requirement for field work is still present, although laboratory analyses are not needed.

The use of spectral measures collected from Landsat TM satellite images similarly provides two methods for identifying sensitive lakes. The cluster analysis grouped the lakes into high and low classes, and produced the same grouping using both the raw and the atmospherically corrected data. The lakes were separated in the same configuration as the location of the peak wavelength using ground measures. This indicates that using the satellite data for this purpose is as advantageous as using the ground measurements. Two regression equations were created, but the equation using the raw image data exhibited the highest r^2 value (0.72) and therefore the most accurate prediction of DOC concentrations. This method has lower predictive power than using the ground measures, but does not require field work or laboratory analysis.

The third procedure used landcover classification to predict the concentration of DOC in lakes in Kejimikujik. A regression equation developed using these data had a r^2 equal to 0.41. Although this method has lower predictive power, the procedure helped to identify the possible sources of DOC from the terrestrial portion of the lake watershed. The three variables identified to have the most significant impact on DOC concentrations were flushing rate, and the area of deciduous forest and open area located within the lake watershed. The ability for prediction may be improved by using a landcover classification produced using a larger scale that may capture more variations in landcover than the Landsat classification.

All three procedures tested in this project proved to be successful at predicting DOC concentrations in varying degrees and DOC was shown to be a good surrogate for mercury concentrations within Kejimikujik National Park ($r^2 = 0.86$). This method could potentially be used by scientists in Kejimikujik concerned with identifying lakes that are

sensitive to mercury pollution. Using the satellite imagery eliminates the need for both field work and laboratory analysis, which can result in quicker and less expensive analysis. Once identified these lakes can then be examined more closely with regards to their mercury content and the biogeochemical processes that are occurring within the lakes.

6.0 References

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7.0 Appendix 1

Spectral curves from 11 lakes in Kejimikujik National Park gathered from field spectroradiometer measurements.

Big Dam East Lake

Big Dam West Lake

Cobrielle Lake

North Cranberry Lake

Pebbleloggitch Lake

Peskawa Lake