DETECTION OF METAL STRESS IN Boreal Forest Species
Using the 0.67 μm ChlOROPHYLL Absorption Band**

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ABSTRACT
Several recent studies have shown that a shift of the red-edge inflection near 0.70 μm in vegetation reflectance spectra is an indicator of metal stress, partially attributable to changes in chlorophyll concentration. This “red-edge shift”, however, is difficult to detect and has been reported both toward longer (red) and shorter (blue) wavelengths. Our work demonstrates that direct measurement of the depth and width of the chlorophyll absorption band at 0.67 μm using digital feature extraction and absorption band characterization procedures developed for the analysis of mineral spectra is a more consistent indicator of metal stress. Additionally, the magnitude of these parameters is generally greater than that of the red edge shift and thus should be more amenable to detection and mapping using field and aircraft spectrometers.

1.0 INTRODUCTION
Many studies have shown that vegetation that has been geochemically stressed will respond with changes in spectral reflectance (Gates, 1965; Collins, 1978; Horler et al., 1980; Collins et al., 1983; Singhroy et al., 1986; Singhroy, 1987). These changes have been observed at the green reflectance peak near 0.57 μm, the chlorophyll absorption maximum near 0.68 μm, and in the reflectance of the infrared reflectance shoulder between 0.75 and 1.1 μm. Stress in plants can result in chlorosis (chlorophyll loss). This phenomenon has been documented in reflectance spectra as the “red-edge shift”, a change in the wavelength position of the inflection point that occurs between 0.68 and 0.75 μm in green vegetation spectra. Stress-induced shifts in the red-edge have been reported both toward longer (red) and shorter (blue) wavelengths, and have been attributed to changes in chlorophyll concentration (Collins et al., 1983; Horler et al., 1983; Rock et al., 1988; Singhroy et al., 1989).

Results of an investigation of ozone-stressed Ponderosa Pine in the Sierra Nevada, California, USA, indicate that although the red-edge is, in part, controlled by chlorophyll concentration, it is also influenced by the condition of the chloroplast membranes on which the chlorophyll is bound (Ustin et al., 1988; Curtiss and Ustin, 1989). The broadening of the chlorophyll absorption bands is attributed to disruption of the membranes. It was suggested that the position of the red-edge shifts to either red or blue wavelengths depending on whether the membrane disruption or the chlorophyll loss process dominates.

Unfortunately, observation and measurement of the red-edge shift is difficult, requiring very high spectral resolution. Differences in wavelength position between stressed and healthy vegetation range from 0 (no shift) to 10 nm, but generally are less than 5 nm (Singhroy et al., 1989). This precludes detection of the red-edge shift with many field spectrometers and most aircraft spectrometers.

Because the chlorophyll concentration is a well defined parameter that has a direct effect on reflectance spectra, we theorized that absorption band analysis techniques developed for extraction and characterization of spectral features from field and laboratory reflectance spectra of minerals would be applicable to analysis of vegetation spectra. These methods have been in use for several years for mineralogical analysis (Green and Craig, 1985; Kruse et al., 1985; Yamaguchi and Lyon, 1987; Clark et al., 1987). They use numerical analysis and characterization of digital reflectance measurements to establish quantitative criteria for identifying minerals and mineral mixtures. This study consisted of re-examining existing spectral measurements of vegetation to determine if in fact the mineral analysis techniques were applicable.

2.0 SPECTRAL ANALYSIS TECHNIQUES

The absorption feature information is extracted from each spectrum using the following automated techniques (Kruse et al., 1988; 1990). A continuum is defined for each spectrum by finding the high points (local maxima) and fitting a continuum of straight line segments between these points (Figure 1A). The continuum is divided into the original spectrum to normalize the absorption bands to a common reference. Portions of the spectrum where the continuum matches the original reflectance are normalized to a value of one, while areas with absorption features have values less than one but greater than zero. The minima of the continuum-removed spectrum are next determined and the strongest absorption features are extracted. The wavelength position, depth, full width at half the maximum depth (FWHM), and asymmetry for each feature are then determined and tabulated (Figure 1B). The asymmetry is defined as the sum of the reflectance values for feature channels to the right of the minimum divided by the sum of the reflectance values for feature channels to the left. The logarithm of this value is taken to linearize the values. Symmetrical bands have an asymmetry value of zero. Bands that are asymmetrical towards shorter wavelengths have negative asymmetries, while bands that are asymmetrical towards longer wavelengths have positive asymmetries. Using this definition, the 0.67 μm chlorophyll absorption band characteristically has negative asymmetry. These techniques have been used successfully for several years to characterize mineral reflectance spectra.

A.

![Figure 1A] Fitted continuum for vegetation spectrum.

B.

![Figure 1B] Continuum-removed spectrum and absorption band parameters. Position is marked by vertical tick.
3.0 RELATION BETWEEN CHLOROPHYLL AND 0.67 μm ABSORPTION BAND PARAMETERS

Ustin and Curtiss (1989) have demonstrated that forest decline symptoms caused by air pollution can be detected using reflectance spectroscopy. Their research used the Jet Propulsion Laboratory (JPL) Portable Instantaneous Display and Analysis Spectrometer (PIDAS) to examine forest decline caused by ozone pollution to Ponderosa Pine (Pinus ponderosa) in the southern Sierra Nevada, California, USA. They observed that moderate levels of ozone exposure resulted in needle chlorosis, premature foliar loss, and altered canopy architectures. To assess the damage, they clustered pine needles according to year of development into “whorls” and visually estimated ozone damage based on the presence of chlorotic banding and mottling. Chlorophyll a, b, and total chlorophyll were determined for each whorl for two sites (sites 12 and 14, Ustin and Curtiss, 1989). Both sites were rated as moderately damaged by ozone with site 12 having a slightly higher damage rating than site 14 (75% vs 60% of branches with chlorotic mottle or banding). Reflectance spectra of uniformly bundled packets of needles were measured for each whorl-age from 0.40 to 2.45 μm using the PIDAS. It was observed that ozone damage appeared to increase with increasing age of the whorls (higher whorl number), and that the position of the reflectance red-edge inflection point near 0.70 μm shifted to shorter wavelengths with increasing damage (decreased chlorophyll concentrations). Similar observations of the red edge shift have been reported by Collins (1978), Chang and Collins (1982), and Rock et al. (1988).

Brian Curtiss (CSES/University of Colorado) provided us with the PIDAS digital spectral data to test weather the feature extraction and absorption band characterization software CSES has developed for mineral analysis would be able to detect the vegetation spectral changes caused by the ozone damage. Figure 2A shows several Ponderosa Pine reflectance spectra for site 12 from 0.50 to 0.80 μm. Note that in general, it can be observed that the older whorls (higher whorl number) have higher reflectance in the 0.67 μm region, however, the position of the red-edge near 0.7 μm visually appears very similar for all spectra. Previous assessments of vegetation health and vigor have relied on detecting this very small shift in the position of the red edge, however, results have been variable and it is not clear weather this shift will be observable using present field spectrometer technology or imaging spectrometers such as AVIRIS and HIRIS. Application of the continuum removal and feature extraction procedures to the spectral data, however, emphasizes the relationship between the whorl age and the reflectance spectra (Figure 2B).

Figure 2. A. PIDAS reflectance spectra from site 12 of Ustin and Curtiss (1989). B. Continuum-removed spectra from site 12. Note decreased absorption band depth of more severely damaged, older growth (whorl 4, S12W4).
The whorl age is seen to be closely related to the depth of the absorption feature at 0.67 μm. This feature can be directly related to the chlorophyll concentration in the vegetation (Salisbury and Ross, 1969; Thomas and Oerther 1972; Tsay et al., 1982; Ustin and Curtiss, 1989). Compare the correlation of R²=0.753 to the total chlorophyll concentrations as measured by Ustin and Curtiss (1989) for the red-edge inflection (Figure 3A) to the very high correlation (R²=0.985) of the 0.67 μm band depth as calculated by the feature analysis software (Figure 3B). The band width at half the absorption feature depth (FWHM) is also closely related to the chlorophyll content (R²=0.820). Although this represents a limited number of analyses (N=6), we conclude from the excellent linear fit of these data that the feature extraction procedure does provide a means of estimating chlorophyll variation caused by vegetation stress. This work suggests that directly characterizing the absorption band itself rather than a subtle shift in the absorption edge may be a better indicator of the vegetation stress exhibited as chlorophyll loss.

\[ y = 0.68719 + 1.1579e-5x \quad R^2 = 0.753 \]

\[ y = 0.02106 + 0.5789e-5x \quad R^2 = 0.985 \]

**Figure 3.**

A. Correlation of Red-Edge Inflection wavelength position with total chlorophyll for whorls 2 through 4 at sites 12 and 14 of Ustin and Curtiss (1989).

B. Correlation of 0.67 absorption band depth with total chlorophyll for whorls 2 through 4 at sites 12 and 14 of Ustin and Curtiss (1989). Note direct relationship. Samples with more chlorophyll correspond to spectra with deeper absorption bands.

### 4.0 CANADIAN TEST SITES AND COLLECTION OF SPECTRA

#### 4.1 TEST SITES

Four test sites in the Canadian Shield were selected for further to study the effect of metal-induced stress. These represented a variety of bedrock and mineralization types, however, in all cases, surficial geology consisted of a thin veneer of locally-derived basal till resting unconformably on mineralized bedrock. Figure 5 shows the locations of the 4 sites.
Figure 4. Test site locations. 1) Arnprior site, 2) Natal Lake site, 3) Atikokan Iron Mine, 4) Capreol Massive Sulfide - approximately located.

4.1.1 Arnprior Site
This site represents a Mississippi-valley-type deposit, with open-space-filling veins crosscutting both Precambrian basement and Paleozoic rocks. Mineralization includes sphalerite, galena, fluorite, barite, and pyrite (Singhroy et al., 1989). Geochemical analysis showed anomalous values over the veins of Zn (106 ppm), Pb (1490 ppm), and Pb (190 ppm). Background areas had values of 11 ppm Zn, and < 10 ppm Pb. Detailed geologic information is included in Springer et al. (1989). Species on this site included Trembling Aspen (Populus tremuloides), White Birch (Betula papyrifera), and Red Oak (Quercus borealis).

4.1.2 Natal Lake
This site is in the Abitibi greenstone belt and consists of mafic to felsic metavolcanics associated with both ultrabasic and felsic intrusive rocks (Carter, 1976; Singhroy et al., 1989). Geochemical assays showed > 300 ppm Zn, > 400 ppm Cr, and > 500 ppm Ni, while the background sites were in the range of < 100 ppm Ni, < 200 ppm Cr, and < 100 ppm Zn. Species on this site consisted of Black Spruce (Picea mariana), and Jack Pine (Pinus banksiana).

4.1.3 Atikokan Iron Mine
The Atikokan site is within the Quetico Greenstone Belt. Geochemical analyses show > 5% Fe, 1% Mg, 500 ppm Mn, and 100 ppm Zn. Species on this site consisted of White Birch, Trembling Aspen, Jack Pine, and Balsam Fir.

4.1.4 Capreol Massive Sulfide
No information was available on this deposit at the time this paper went to press. It is assumed from the results of the spectral analyses that there are concentrations of heavy metals such as Pb and Zn at the site. Species measured consisted of White Birch and White Pine.
4.2 COLLECTION OF SPECTRA

Because most areas of the Canadian Shield are covered by glacial drift and dense vegetation, conventional remote sensing techniques for prospecting for mineral deposits and geologic mapping are marginally useful. As a result, experimental work in Canada on the use of remote sensing for exploration has focused on identifying characteristic spectral responses of geochemically stressed vegetation using laboratory, field, and airborne spectral data as proximal indicators of mineralization. As part of this research program, digital laboratory spectra for trees from the Canadian boreal forest have been obtained over the last several years by the Ontario Centre for Remote Sensing for trees growing both on non-mineralized and mineralized ground (areas with anomalous concentrations of various metals). The spectra used here were measured on a SE590 laboratory spectrometer manufactured by Spectron Engineering, Inc at 2.8 nm resolution over the 0.4 to 1.1 μm range with respect to a BaSO₄ reflectance standard.

Vegetation sampling was conducted in July and August, prior to fall senescence. Leaves were taken from the crown and outer branches of the most abundant tree species at each site. They were placed in plastic bags within a dark cooler to prevent moisture loss and continued photosynthesis after cutting, and measured using the SE590 within 5 hours (Singer et al., 1989). The spectrometer was mounted 15 cm over the target and a tungsten halogen 600 watt light source oriented at 80 degrees to the horizontal was used. Three or more layers of deciduous leaves or four to five layers of conifer twigs were stacked to cover a 30 x 15 cm black plate, more than filling the 6 x 6 cm FOV of the instrument. Spectra used for the analysis were the averages of from 6 to 15 spectra.

5.0 ANALYSIS OF THE 0.67 μm ABSORPTION BAND FOR THE 4 SITES

Spectra of the four sites were analyzed by first calculating an average background and mineralized spectrum for each species at each site. A total of 22 average spectra representing over 225 individual spectra for 7 different species were analyzed, along with spectral variation for the averages. The average spectra were analyzed using the feature extraction software described in Section 2 above. An example of a spectrum for background and mineralized red oak (Quercus borealis) and the corresponding continuum-removed spectra for Site 1 are shown in Figure 5. The position of the red-edge inflection was also calculated for each of the average spectra.

A. 

![Graph A]

B. 

![Graph B]

Figure 5. A. Spectrum of Red Oak for Site 1. B. Continuum-removed spectrum, Site 1.
Based on our experience during 1989 with the ozone-damaged Ponderosa Pine needles, which showed a high correlation between total chlorophyll and the 0.67 μm absorption band depths and widths, we expected that we would be able to detect and characterize any damage or stress caused by the exposure to mineralized soils at the 4 sites. Additionally, we expected that the depth of the 0.67 μm band would be a better indicator of metal-induced stress than the red-edge inflection. Figure 6A shows the position of the red-edge inflection for each of the species at the 4 sites. Note that the red-edge shift, if present, is very small and that it occurs both toward the blue and towards the red. When the feature extraction procedures are used to characterize the chlorophyll absorption feature near 0.67 μm the trend is much more consistent (Figure 6B). The 0.67 μm band depth is an excellent indicator of stress in nearly all cases, even though the mineralization causing the stress at each of the sites is quite different. It is consistent across several species, including both evergreen and deciduous types. Figure 7 clarifies the response of the vegetation to metal-induced stress as measured by both the red-edge inflection and the 0.67 μm absorption band depth. Figure 7A illustrates that for most cases (6 of 11) the red-edge inflection shifts to shorter wavelengths, that is towards the blue. This is the so called "blue shift" of the red edge. Note, however, that the shift is toward longer wavelengths (red) for both occurrences of Jack Pine (Pinus banksiana) and that there is no shift for three of the background/mineralized sets. Note also that the largest shift is approximately 0.009 μm (9 nm). In most cases (8 of 11), the shift is less than 0.004 μm (4 nm). Figure 7B shows the calculated 0.67 μm absorption band depth for the same spectra. It is apparent that this parameter is a good indicator of metal-induced stress, with the band typically becoming shallower for the mineralized samples with respect to background (9 of 11). Note the reversal of this trend in two cases at Site 3 (Atikokan Iron Mine). In addition, the 0.67 μm absorption band width (FWHM) is also a good indicator of vegetation stress (Figure 8). The FWHM decreases with stress for most of the measurements (8 of 11).

Figure 6A. Relationship between vegetation stress and red-edge inflection. Inflection shifts to shorter wavelengths in 6 of 11 mineralized cases.

Figure 6B. Relationship between vegetation stress and 0.67 μm absorption band depth. Band depth is less in 9 of 11 mineralized cases.
Figure 7A. Red-edge shift for stressed vegetation. Note that all shifts are less than 0.010 µm (10 nm).

Figure 7B. Percent change in depth at 0.67 µm with stress.

Figure 8A. Plot showing relationship of 0.67 µm absorption band width (FWHM) to vegetation stress. In 8 of 11 cases, the mineralized sites have a lower FWHM (a narrower band).

Figure 8B. Percent change in FWHM with stress.
6.0 DISCUSSION

Clearly, the 0.67 μm absorption band depth and FWHM are excellent indicators of metal-induced stress. The two cases where the band depth appears to fail by showing increased depth for what should be stressed trees can be explained by examining the nature of the mineralization, and the variability of the spectra. It is suggested that this apparent reversal in the trend of the 0.67 μm band depth measurements can be explained by the > 5% Fe at Site 3 (Atikokan Iron Mine). Fe is a macronutrient and may cause the deciduous trees to appear healthier than the coniferous species. Spatial variability of this nutrient may also explain the high variability for the spectra at these sites. Figure 9 shows the variability of spectral reflectance at 0.7801 μm (the IR plateau), 0.6702 (the chlorophyll absorption band), and 0.5504 μm (the green peak). Note that both of the failures occur for average spectra that have the highest variability. The trembling aspen at Site 3 (Atikokan Iron Mine) background, has the highest variability of all samples at 0.7801 μm. The white birch at Site 3 has the highest variability of the mineralized areas, again at 0.7801 μm.

Figure 9A. Plot showing spectral variation from the mean for all species - background.
Figure 9B. Plot showing spectral variation from the mean for all species - mineralized.

7.0 CONCLUSIONS

Plots of the red-edge inflection versus total chlorophyll concentration for ozone-stressed Ponderosa Pine in the Sierra Nevada, California, USA, give a correlation of R²=0.753 while similar plots of the 0.67 μm band depth show a correlation of R²=0.985. This establishes the strong link between the absorption band depth and chlorophyll concentration. Additional testing using this method using several boreal forest species in northern Canada show that the red-edge inflection or red-edge shift is inconsistent, not a very good indicator of stress. The shift, when present, is very small and occurs both towards the blue and the red. The magnitude of this shift is
such that it will preclude detection using many laboratory and field spectrometers and most aircraft spectrometers. The changes in the 0.67 μm chlorophyll band, however, follow a consistent trend in which the band is typically shallower and narrower for both deciduous and coniferous metal-stressed species. Because the measurement is one of the depth of the reflectance spectra rather than the exact position of a subtle inflection, it is easier to calculate, and appears to be independent (to the first order) of the spectral resolution of the sensor. Thus, it should be more amenable to detection and mapping using field and aircraft spectrometers.

8.0 ACKNOWLEDGMENTS

Portions of this work were completed while the 1st author (Singhroy) was at the Ontario Center for Remote Sensing. Development of the feature extraction and absorption band characterization techniques and analysis of these data was supported by NASA Grant NAGW-1601. We thank Dr. Brian Curtiss at CSES for providing the digital PIDAS spectra and chlorophyll data that allowed quantification of the relationship between chlorophyll concentration and the absorption band depth.

9.0 REFERENCES

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